

OXIDATIVE-ADDITION REACTIONS OF ORGANIC HALIDES AND INTERHALOGENS  
WITH TETRAKIS(TRIPHENYLPHOSPHINE)PLATINUM(0)

BY

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A DISSERTATION PRESENTED TO THE GRADUATE  
COUNCIL OF THE UNIVERSITY OF FLORIDA IN PARTIAL  
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1974

## DEDICATION

The author proudly dedicates this dissertation  
to his mother and to the memory of his father.

"I can see farther because I stand on the shoulders  
of giants."

Issac Newton

## ACKNOWLEDGMENTS

The author wishes to express his appreciation to his research director, Dr. Carl Stoufer, for his interest, support and guidance for the duration of this work. Thanks are also due to Dr. George Ryschkewitsch and Neil Weinstein for stimulating and helpful discussions.

The author wishes to thank Dr. John F. Baxter who taught him how to teach and in the process imparted much chemical knowledge.

Gratitude is also expressed to the United States Government for a Fulbright-Hays Award, which enabled the author to study in an American institution.

Finally, the author expresses a very special appreciation and gratitude to his wife for not only typing this manuscript, but above all for her love, patience, understanding, encouragement and support without which this dissertation could not have been written.

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Abstract of Dissertation Presented to the Graduate Council  
of the University of Florida in Partial Fulfillment of the  
Requirements for the Degree of Doctor of Philosophy

OXIDATIVE-ADDITION REACTIONS OF ORGANIC HALIDES AND INTERHALOGENS  
WITH TETRAKIS(TRIPHENYLPHOSPHINE)PLATINUM(0)

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December, 1974

Chairman: R. Carl Stoufer  
Major Department: Chemistry

The oxidative-addition reactions of some halogens, interhalogens and arylmethyl halides with tetrakis(triphenylphosphine)platinum(0) were investigated. The arylmethyl halides used were triphenylmethyl chloride and diphenylmethyl bromide. Activation parameters for the reaction of tetrakis(triphenylphosphine)platinum(0) with methyl iodide, triphenylmethyl chloride and diphenylmethyl bromide were obtained. The values of the second-order rate constants at 25°(M<sup>-1</sup>sec<sup>-1</sup>), activation energies(kcal/mole) and entropies of activation(eu), respectively, were determined to be: triphenylmethyl chloride, 2.6 x 10<sup>-1</sup>, 9.4 and -32; diphenylmethyl bromide, 2.9 x 10<sup>-1</sup>, 8.2 and -32; and methyl iodide, 2.6 x 10<sup>-3</sup>, 5.2 and -54. From these data and other evidence, a free-radical mechanism for the oxidative addition of aromatic tertiary and secondary halides is proposed.

Several 4-pyridyldiarylmethyl chlorides and their palladium(II) complexes were synthesized. It was discovered that the reaction of these compounds with tetrakis(triphenylphosphine)platinum(0) provided a rapid method of generating 4-pyridyldiarylmethyl radicals.

The oxidative-addition reaction of iodine monochloride to

tetrakis(triphenylphosphine)platinum(0) was found to yield cis-chloriodobis(triphenylphosphine)platinum(II), trans-diiodobis(triphenylphosphine)platinum(II) and trans-dichlorobis(triphenylphosphine)platinum(II), respectively, when the mole ratio of the Pt(0) complex to interhalogen was 1:1, 1:3 and 1:6. The formation of such diverse products merely by changing the stoichiometric amounts of the two reactants was successfully rationalized and a mechanism for the initial oxidative addition of iodine monochloride to tetrakis(triphenylphosphine)platinum(0) is proposed. This mechanism predicts the oxidative addition of iodine, bromine and chlorine to tetrakis(triphenylphosphine)platinum(0) would give trans-dihalogenobis(triphenylphosphine)platinum(II), in direct conflict with numerous reports of the isolation of cis-isomers in the literature. These predictions were verified under carefully controlled conditions.

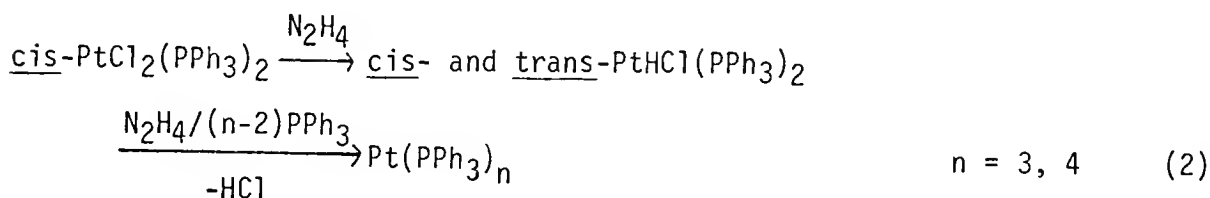
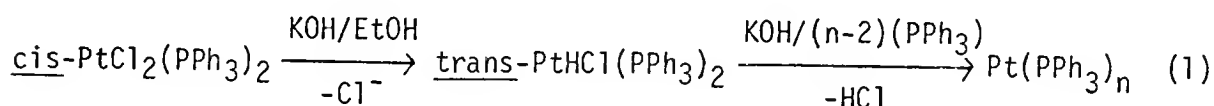
Iodine monobromide and iodine monochloride were found to react analogously towards tetrakis(triphenylphosphine)platinum(0).

Many reactions of halogens and interhalogens with  $\text{PtX}_2(\text{PPh}_3)_2$  and  $\text{PtXY}(\text{PPh}_3)_2$ , where X and Y = Cl, Br or I, were found to be facile substitution reactions.

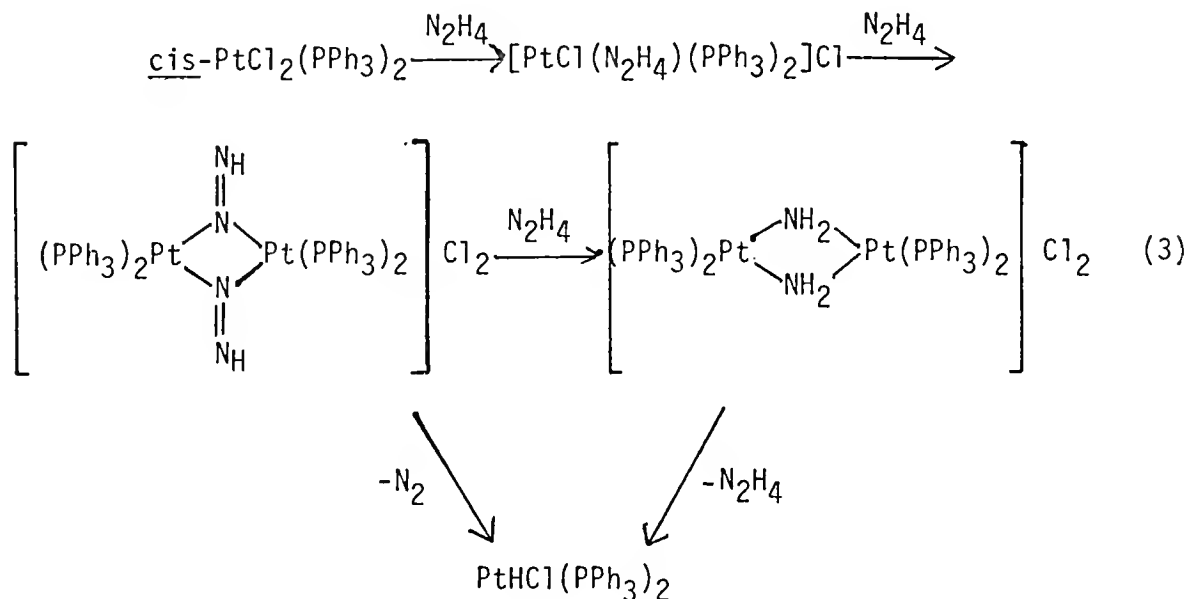
## INTRODUCTION

Platinum(0) complexes containing triphenylphosphine and related ligands were first synthesized by Malatesta and co-workers<sup>1,2</sup> nearly 17 years ago by reduction of platinum(II)-phosphine complexes with hydrazine, alcoholic potassium hydroxide and excess triphenylphosphine. It was first contended<sup>3,4</sup> that these were hydrido-complexes of platinum(II) with coordination numbers of 5 or 6 because hydrido-complexes had been obtained under similar reduction conditions and because of the similar stabilities with respect to oxidation. Between 1961 and 1963 several groups of workers<sup>5,6,7</sup> demonstrated conclusively that these complexes were bona fide zero-valent compounds (defined as compounds having zero oxidation states) rather than hydrido-complexes; and since then, much attention has been devoted to the chemistry of zero-valent metal complexes.

It is now known that the first stage of the reduction of these triphenylphosphine-platinum(II) complexes is the formation of a hydrido-complex of platinum(II); in the second stage, the reducing agents, also bases, dehydrogenate the species:

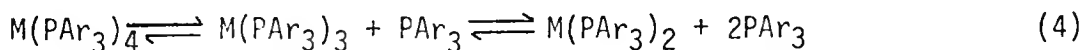


The detailed mechanism of these reductions is complex but some labile intermediates in the hydrazine reduction have been isolated<sup>8</sup> such as that represented below:



As a matter of fact, the isolation of either hydrido-complexes of platinum(II) or platinum(0) depends upon the temperature, the concentration of the reducing agent and upon the reaction time.

Zero-valent compounds dissociate in solution giving rise to coordinately unsaturated species via the equilibrium:



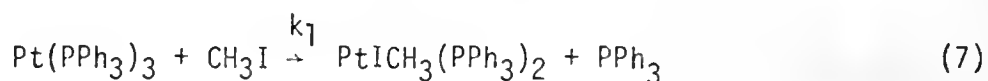
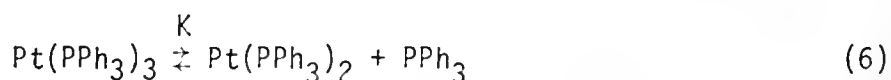
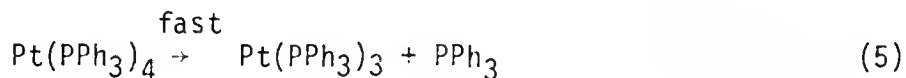
In solution, these low-valent, coordinately unsaturated species such as bis(triphenylphosphine)platinum(0) are solvated centers to which "oxidative addition" is attributed. The term "oxidative addition" is used to designate a broad class of reactions, generally of low-spin, transition metal complexes, in which oxidation (i.e., an increase in the oxidation number of the metal) is accompanied by an increase in the coordination number of the metal.

It has been asserted that the unusual stabilities of the coordinately unsaturated species with respect to tetrakis(triphenylphosphine)-platinum(0) is a consequence of an excess of negative charge on the zero-valent metal.<sup>9</sup> Thus, the small tendency of the metal ion in these zero-valent complexes to increase its coordination sphere arises from an electrostatic repulsion of the  $\sigma$ -electron pair of the free ligands by the non-bonding electrons on the metal. The basic properties of some  $d^{10}$ , zero-valent systems have been demonstrated recently<sup>10</sup> in complexes with phosphines in which stable hydrido-compounds such as  $\text{Pt}(\text{H})(\text{X})(\text{PPh}_3)_2$  are formed with acids  $\text{HX}$  where  $\text{X} = \text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_4^-$ . Thus, ligands which increase the electron density on the metal atom cause the metal to be more susceptible to oxidative addition reactions which results in the relieving of the high electron density on the metal atom. Conversely, ligands which decrease electron density at the central metal atom decrease the tendency of the metal to undergo oxidative addition. Indeed, Nixon and Sexton<sup>11</sup> have found no evidence for the formation of any tri- or dicordinate fluorophosphine platinum(0) species (fluorophosphine =  $\text{PF}_3$ ,  $\text{CF}_3\text{PF}_2$  or  $(\text{CF}_3)_2\text{PF}$ ) in a solution of the tetra-coordinate complexes. Moreover, in contrast to the triphenylphosphine platinum(0) complexes, the fluorophosphine analogs do not react with alkyl halides and hydrogen chloride. This difference in behavior is attributed to the differing donor and acceptor abilities of the ligands. With fluorophosphines which are weaker  $\sigma$ -donors but stronger  $\pi$ -acceptors than triphenylphosphine, the electron density at the metal is lowered, thus reducing its tendency to dissociate and to undergo oxidative-addition reactions.

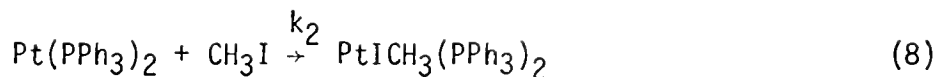
The major effort of research activity on zero-valent complexes has been concerned with the preparations and reactions

of complexes of diverse types and with the elucidation of structures. Complexes with many different and often novel types of organic and inorganic ligands have been conveniently synthesized by utilizing oxidative-addition reactions. Indeed, many of the products formed are inaccessible by other synthetic routes. For a  $d^{10}$  configuration, such as that represented by tetrakis(triphenylphosphine)platinum(0), oxidative-addition reactions are known in which halogens, metal halides, alkyl halides, aryl halides, acyl halides, sulfonyl halides, inorganic and organic acids, and other organic molecules serve as the oxidants. Relatively few mechanistic studies on these reactions have been reported. Furthermore, the dependence of reactivity upon the electronic and structural factors of reacting species is, in the main, still not well understood.

The oxidative addition of methyl iodide to tetrakis- and tris(triphenylphosphine)platinum(0) yield the  $\sigma$ -organometallic compound of the type  $PtICH_3(PPh_3)_2$ <sup>12,13</sup>. This type of reaction has been extended to methyl, styryl and cyclohexyl bromides<sup>14</sup>; benzyl<sup>15</sup>, phenyl and perfluoroalkyl halides<sup>16</sup>. Pearson and Rajaram<sup>17</sup> have reported the oxidative addition of methyl iodide to tetrakis- and tris(triphenylphosphine)platinum(0). They found that there is a preliminary dissociation of tetrakis(triphenylphosphine)platinum(0) yielding unsaturated, solvated species which subsequently react with the methyl iodide:

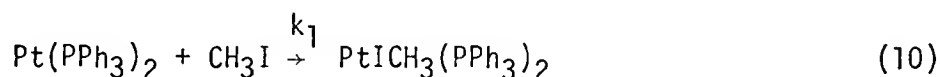
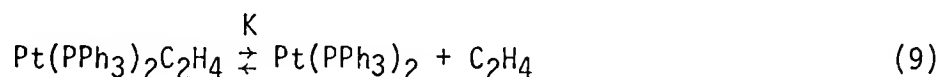




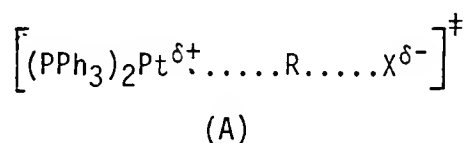


From the kinetic data, they estimated  $k_1$  and  $k_2$  to be  $3.5 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$  and  $2.0 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ , respectively.

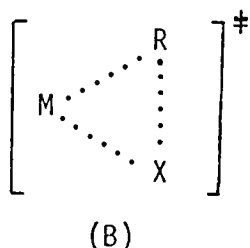
A similar mechanism is proposed<sup>15</sup> in the oxidative-addition reactions between ethylenebis(triphenylphosphine)platinum(0) and methyl bromide, benzyl bromide and ethylene diiodide (which gives ethylene and the diiodo-complex):



Although the overall reaction scheme has been established for these compounds, nothing is yet known of the nature of the transition state for the alkyl halide addition to bis(triphenylphosphine)platinum(0). Cook and Jauhal<sup>14</sup> have proposed that there is an intermediate or transition state of the type (A) by analogy with the iridium(I) addition reactions<sup>18</sup>.



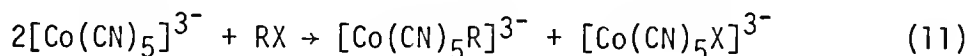
Another feasible polar mechanism can involve transition state of type (B), which is a transition state of low polarity in which two addendum



atoms interact with the metal simultaneously. However, Pearson and

Rajaram<sup>17</sup> found that, in the case of methyl iodide and tetrakis(tri-phenylphosphine)platinum(0), the rate of reaction increases with an increase in the polarity of the solvent, an observation consistent with a dipolar transition state (A).

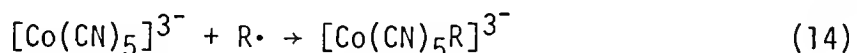
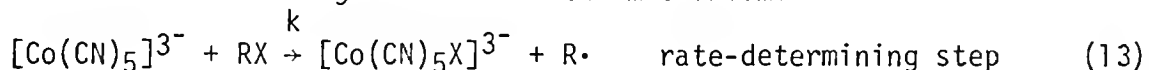
Two-electron oxidations of  $\text{Pt}(\text{PPh}_3)_3$  by primary alkyl halides have been reported based on spin-trapping experiments,<sup>19</sup> but the results have been invalidated.<sup>20</sup> However, Halpern and his co-workers<sup>21,22</sup> and others<sup>23</sup> have demonstrated that alkyl radicals are involved in the one-electron oxidations of  $\text{Co(II)}$  complexes with alkyl halides,  $\text{RX}$ , to give  $\text{Co(III)}$  alkyl compounds. The stoichiometry of the reaction



and the rate law

$$-d[\text{Co}(\text{CN})_5]^{3-}/dt = 2k[\text{Co}(\text{CN})_5]^{3-}[\text{RX}] \quad (12)$$

were shown to be in agreement with the mechanism:

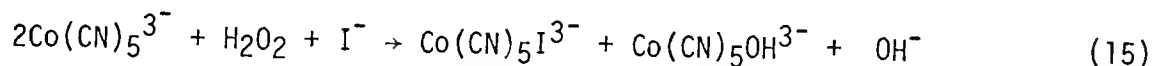


The evidence cited for the proposed mechanism<sup>22b,23</sup> is as follows:

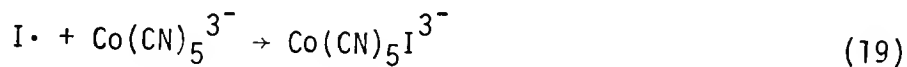
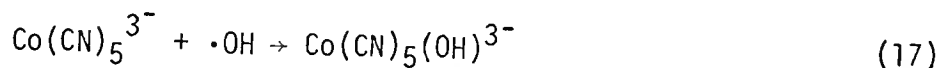
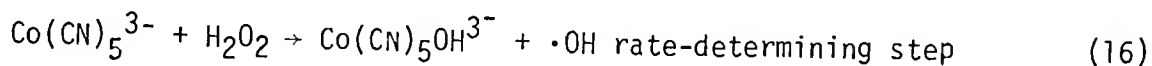
(1) The isolation of alkyl-acrylonitrile adducts from the reaction of *n*-propyl or isopropyl iodide with pentacyanocobaltate(II) in the presence of excess acrylonitrile indicate the scavenging of alkyl radical intermediates. (2) Dimeric species presumably from free-radical precursors were found in reactions where the oxidizing agents were trityl and tropylium halides. (3) When benzenediazonium chloride was the oxidizer, nitrogen was evolved and a complex was formed which appeared to contain a phenyl-cobalt bond. In similar processes, aryl radicals are known to be involved.<sup>24</sup> (4) The observed reactivity pattern of pentacyanocobaltate(II) toward alkyl halides was found to exhibit an inverse dependence

on the carbon-halogen bond (i.e.,  $k_{R-Cl} < k_{R-Br} < k_{R-I}$ ), an observation compatible with the proposed mechanism. (5) The observed trends in rate constants ( $k_{X-CH_2CH_2COO^-} < k_{X-CH_2COO^-}$ ) reflect greater stability of the resulting free-radical; trends analogous to those in (4) and (5) have been found for the rates of halogen abstraction from organic halides by sodium atoms<sup>25</sup>, and by organic free radicals<sup>26</sup>.

The oxidation of pentacyanocobaltate(II) by hydrogen peroxide, hydroxylamine and cyanogen iodide has been proposed<sup>27</sup> to proceed by an analogous free-radical mechanism. Halpern and co-workers found that the presence of an added amount of iodide ion did not affect the rate of the reaction between pentacyanocobaltate(II) and hydrogen peroxide, but it did alter the stoichiometry of the reaction which is:

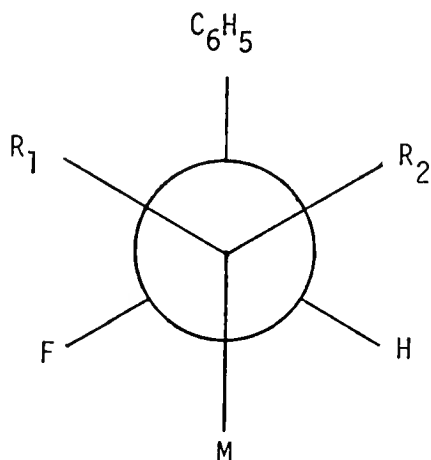


They contended that the iodide ion acted as a scavenger for the hydroxyl radicals and that the resulting iodine atom subsequently reacted with pentacyanocobaltate(II) to yield pentacyanoiodocobaltate(III). The mechanism of the reaction is thus:



The only other postulated free-radical mechanism found in the literature<sup>28</sup> involves the two-electron oxidation of the primary halides

II a-c to trans-chlorocarbonylbis(triphenylphosphine)iridium(I) resulting in III



II, M = Br

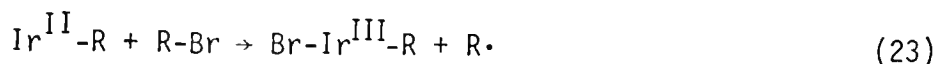
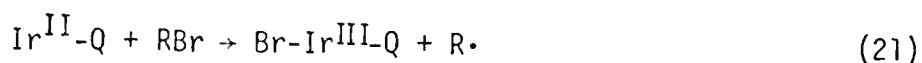
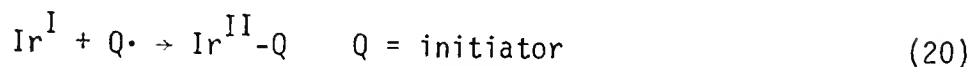
a,  $R_1 = R_2 = H$

b,  $R_1 = H$ ;  $R_2 = D$

c,  $R_1 = D$ ;  $R_2 = H$

III, M =  $\text{IrBrCl}(\text{CO})(\text{PMe}_3)_2$

A mechanism for the oxidative addition to  $\text{Ir(I)}$  was proposed from the



following:

(1) The rate of addition is enhanced by free-radical initiators such as benzoyl peroxide but is retarded by radical scavengers. (2) There is racemization at the carbon atom in the products III, an observation consistent with reaction (21) and (22). (3) Competitive experiments

indicate that the rate is enhanced by electron-withdrawing substituents in the organic halide. This observation has precedence in related radical processes involving alkyl halides.<sup>29</sup>

Although the reaction of tetrakis(triphenylphosphine)platinum(0) with alkyl halides usually results in the addition of both the halogen and the alkyl moiety to the platinum atom, it was found in some cases that cis-dihalogenobis(triphenylphosphine)platinum(II) is formed. This was observed in the reaction of the platinum(0) complex with carbon tetrachloride,<sup>30,31</sup> cis-1,2-dichloroethylene,<sup>14</sup> hexachloroethane,<sup>14</sup> chloroform<sup>14</sup> and bromotrichloromethane.<sup>14</sup> Another peculiarity is that, whereas, tetrakis(triphenylphosphine)platinum(0) has been reported by Cook and Jauhal<sup>14</sup> to react smoothly with trityl bromide to yield the usual organobromo-platinum(II) complex, the same reaction with trityl chloride yields trityl free-radicals and dichlorobis(triphenylphosphine)-platinum(II).<sup>19</sup> The factors which favor one organic halide to react to yield the usual organohalogeno-platinum(II) complex from the reaction with tetrakis(triphenylphosphine)platinum(0) and another analogous halide to yield cis-dihalogenobis(triphenylphosphine)platinum(II) should be investigated.

In the case of the reaction of tetrakis(triphenylphosphine)-platinum(0) with carbon tetrachloride, cis-dichlorobis(triphenylphosphine)platinum(II) and hexachloroethane are formed. One might propose that the reaction first involves an oxidative addition to form the normal platinum(II) complex,  $\text{PtCl}(\text{CCl}_3)(\text{PPh}_3)_2$ , followed by another oxidative addition to form a platinum(IV) species which subsequently undergoes a reductive elimination yielding the final products.

In the light of these and similar observations, it seems to be

of interest and of importance to investigate and attempt to elucidate the mechanism of the reactions between selected organic halides and tetrakis(triphenylphosphine)platinum(0) which yield dichlorobis(triphenylphosphine)platinum(II) and other products and also to determine if this behavior arises as a consequence of a new free-radical pathway. Such an investigation should include kinetic studies of the reactions and the evaluation of activation parameters from which data on the nature of the transition states may be inferred. Further, an attempt to correlate reactivity and mechanism with structural aspects of the addendum molecule would shed more light on these oxidative-addition reactions. This work will be extended to the investigation of  $d^8$  systems such as Rh(I) and Ir(I) and a comparison of the reactions and mechanisms with those of  $d^{10}$ , platinum(0) systems.

The work of Lappert and Lednor<sup>19</sup> involving the reaction of tetrakis(triphenylphosphine)platinum(0) with trityl chloride to form trityl radicals and cis-dichlorobis(triphenylphosphine)platinum(II) was repeated and confirmed. Logically, the report of Cook and Jauhal involving the reaction of tetrakis(triphenylphosphine)platinum(0) with trityl bromide was also repeated in this laboratory but no organohalogeno-platinum(II) complex could be isolated as claimed by the authors; instead trityl radicals and cis-dibromobis(triphenylphosphine)platinum(II) were formed as is to be expected by analogy with the reaction using trityl chloride and the platinum(0) complex. Moreover, the rate of these reactions was found to be relatively fast, the reaction being completed in minutes. Thus, it would be useful to investigate the feasibility of the general applicability of this method for the generation of triarylmethyl radicals as this would be an improvement to the classical method of Gomberg<sup>32</sup>

who used molecular silver and the triarylmethyl chloride, a reaction which takes up to 4 days for complete reaction.<sup>33</sup>

Finally, the objective of this work is the synthesis of some 4-pyridyldiarylmethyl and di(2-pyridyl)arylmethyl chlorides and the reaction of these with the platinum(0) complex in the attempted synthesis of the corresponding, hitherto unknown, free-radicals (a reaction analogous to that between platinum(0) complex and trityl chloride) so that their stabilities and other properties can be evaluated.

## EXPERIMENTAL

### Materials

Common chemicals were of reagent grade and were used without further purification unless otherwise specified. Palladium complexes were synthesized according to the method of Richardson<sup>34</sup> by reacting tetrachloroplatinate(II) with the appropriate ligand in methanol. Solvents used in the synthesis of tertiary organic halides and in reactions involving the use of interhalogens were dried by distillation over a suitable drying agent. Iodine monochloride and iodine monobromide were obtained commercially and used without further purification. Chlorocarbonylbis(triphenylphosphine)Ir(I) was also obtained commercially and was recrystallized before use.

### Elemental Analysis

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. All samples for analyses were dried in vacuo at the boiling point of acetone, n-heptane or xylene to remove solvent molecules from the crystals.

### Dry Box

All reactions involved in the synthesis of tertiary organic halides and others requiring a dry or inert atmosphere were carried out in a Vacuum Atmosphere dry box (model: Dri-Train).



### Spectrometers

All infrared spectra were obtained using a Beckman IR-10 spectrophotometer. Samples of the compounds were prepared for analysis as KBr discs.

Visible and ultraviolet spectra were obtained with a Cary 15 recording spectrophotometer. Quartz cells of 1.00 cm path lengths were used.

$^1\text{H}$  nmr spectra were obtained at 60 Hz using a Varian A60-A spectrometer. The chemical shifts are reported in Hz from tetramethylsilane which was used as the internal reference.

Electron spin resonance spectra were obtained using a Varian E-3 model spectrometer.

### Kinetics

All the kinetic measurements were made at 25° in benzene solution unless otherwise stated. The reactions were followed spectrophotometrically using a Cary 15 recording spectrophotometer with the cell holder thermostated to within  $\pm 0.10^\circ$ . The rates of the reactions were measured by following as a function of time the disappearance of the tetrakis(triphenylphosphine)platinum(0) at 415 nm ( $\epsilon 1.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the case of triphenylmethyl chloride and methyl iodide and at 425 nm ( $\epsilon 1.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the case of diphenylmethyl bromide. Customarily, the initial concentrations of the platinum(0) complex employed were between  $5.0 \times 10^{-4}\text{M}$  and  $1.0 \times 10^{-3}\text{M}$ , those of triphenylphosphine between  $1.0 \times 10^{-3}\text{M}$  and  $1.0 \times 10^{-2}\text{M}$  and those of the reacting halide were  $\geq 50$  times that of the platinum(0) complexes to maintain a constant concentration of reacting halide.

Benzene was dried and deoxygenated by distillation over sodium benzophenone ketyl and bubbling a stream of pre-purified nitrogen through the distilling solution. Methyl iodide was distilled under vacuum and degassed by freeze-thawing. The stock solutions were prepared in a dry box and 1 ml of the platinum(0) complex and tri-phenylphosphine solution were pipetted into a 1 cm cuvette which, together with the flask containing the organic halide stock solution, was then sealed with a rubber serum cap. The cuvette and flask and a hypodermic syringe were put into glass tubes immersed in the thermostated water bath for 15 minutes to achieve thermal equilibrium of reactants. Using the syringe, 1 ml of the organic halide stock was quickly transferred to the cuvette and the absorbance was plotted as a function time by the spectrophotometer. A plot of  $\log (A-A_{\infty})$  vs time was found to be linear for at least 75% reaction.

### Syntheses and Reactions

#### Synthesis of 4-Pyridyldiphenylmethyl Chloride

A suspension of 4-pyridyldiphenylmethanol (10 g, 0.038 mole) in 100 ml of carbon tetrachloride was brought to reflux and 9.0 ml of freshly distilled thionyl chloride in 3 ml aliquots was added cautiously at 5-minute intervals. The solid dissolved and the solution was refluxed for one hour after which it was concentrated by distillation to about 20 ml. Addition of benzene and cooling gave crystals of the hydrochloride salt of 4-pyridyldiphenylmethyl chloride. Recrystallization from methylene chloride-benzene afforded 7 g (70%) of colorless crystals, mp  $187^{\circ}(\text{dec.})$ .

To a methylene chloride solution of the hydrochloride salt (6.3 g)

prepared above was added an excess of 2,6-lutidine (12 ml), whereupon colorless crystals of 2,6-lutidinium chloride (mp 234-5° dec) deposited. Petroleum ether (10 ml) was added to effect more complete precipitation of the lutidinium chloride. The precipitated solid was removed by filtration; and the filtrate was evaporated to dryness under reduced pressure to yield 4-pyridyldiphenylmethyl chloride. This could be purified by recrystallization from carbon tetrachloride, petroleum ether or by sublimation in vacuo to give 2.5 g (42%) of product of mp 89.5-90°. Anal. Calcd for  $C_{18}H_{14}NCl$ : C, 77.28; H, 5.04; N, 5.01; Cl, 12.67. Found: C, 77.86; H, 5.08; N, 4.93; Cl, 12.74.

#### Synthesis of 4-Pyridyldi(p-tolyl)methyl Chloride

A stream of dry HCl gas was slowly bubbled through a solution containing 6.0 g (20 mmole) of 4-pyridyldi(p-tolyl)methanol in a mixture containing an equal volume of  $CHCl_3$  and  $CH_2Cl_2$ . After 2.5 hours, the solution was evaporated to dryness under reduced pressure to give the hydrochloride salt of 4-pyridyldi(p-tolyl)methyl chloride. This was recrystallized by dissolving in methylene chloride and precipitating with benzene or n-hexane.

To a solution containing 2.5 g of the above recrystallized hydrochloride in 20 ml of methylene chloride was added 5 ml of 2,6-lutidine. The agitated mixture was allowed to stand for 10 minutes during which colorless crystals of 2,6-lutidinium chloride deposited and was removed by filtration. On concentrating the filtrate under reduced pressure, more 2,6-lutidinium chloride deposited and it was again filtered off. The mixture of solvents was then completely evaporated off under reduced pressure to yield a rather thick and yellowish viscous liquid. After standing the flask over a cold plate,

slightly yellow-colored crystals slowly formed. The solid was broken up with a spatula and washed with a small quantity of cold petroleum ether to give crystals having a melting point of 68-74°. Recrystallization from petroleum ether yielded 1.6 g (72%) of colorless crystals, mp 74-75°. Anal. Calcd for  $C_{20}H_{18}NCl$ : C, 78.04; H, 5.89; N, 4.55; Cl, 11.52. Found: C, 77.94; H, 6.11; N, 4.45; Cl, 11.41.

#### Synthesis of 4-Methyl-2-thiazolyldiphenylmethyl Chloride

To a refluxing solution of carbon tetrachloride (15 ml) containing 4-methyl-2-thiazolyldiphenylmethanol (1.1 g) was added 2 ml of thionyl chloride. After 30 minutes, most of the liquid was distilled off and the solution was evaporated to dryness under reduced pressure to give a pale yellow oil. This was dissolved in a little carbon tetrachloride and on adding petroleum ether and standing on a cold plate, colorless crystals deposited, mp 62-64°. The crude product was then purified by sublimation in vacuo to yield 0.7 g (65%) of pure product, mp 64-65°. Anal. Calcd for  $C_{17}H_{14}ClNS$ : C, 68.10; H, 4.71; N, 4.47, Cl, 11.83. Found: C, 67.88; H, 4.92; N, 4.47; Cl, 11.66.

#### Synthesis of 2-Thiazolyldiphenylmethyl Chloride

A suspension of 2-thiazolyldiphenylmethanol (2.0 g) in 20 ml methylene chloride and 5 ml of carbon tetrachloride was brought to a reflux and 5 ml of thionyl chloride was then added. The solution was refluxed for another 4 hours and the solvent was then evaporated off under reduced pressure to give a purplish and then a greenish gum. After the gum was dissolved in methylene chloride, 5 ml of 2,6-lutidine was added and the solution concentrated to give a white solid which

was removed by filtration. The filtrate was then evaporated to dryness to give a very dark brown solid. To this solid was added 10 ml of carbon tetrachloride whereupon most of the solid dissolved. Activated charcoal was added and this mixture was boiled for 5 minutes. On filtration and concentration of the solvent, petroleum ether was added and the solution was placed on a cold plate. Crystals formed on the side of the flask were separated by filtration and purified by sublimation in vacuo to give a colorless solid, mp 68.5-69.5°. The mass spectrum of the product gave two peaks of mass 287 and 285 corresponding to m/e of the 2-thiazolyldiphenylmethyl chloride ion containing  $^{37}\text{Cl}$  and  $^{35}\text{Cl}$ , respectively. Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{ClNS}$ : C, 67.24; H, 4.23; N, 4.90, Cl, 12.41. Found: C, 67.13; H, 4.27; N, 4.75; Cl, 12.14.

Synthesis of Di(2-pyridyl)phenylmethyl Chloride and Di(2-pyridyl)-(p-methoxyphenyl)methyl Chloride

The reaction between 4.0 g of di(2-pyridyl)phenylmethanol and 8 ml of thionyl chloride gave the hydrochloride of di(2-pyridyl)-phenylmethyl chloride. Treatment of this with excess lutidine and work-up in a similar manner as for the preparation of 2-thiazolyldiphenylmethyl chloride gave colorless crystals of melting point 107.5-108.5°. The mass spectrum of the product gave two peaks of mass 282 and 280 corresponding to m/e of the molecular ion containing  $^{37}\text{Cl}$  and  $^{35}\text{Cl}$ , respectively. Anal. Calcd for  $\text{C}_{17}\text{H}_{13}\text{ClN}_2$ : C, 72.73; H, 4.67; N, 9.98; Cl, 12.63. Found: C, 72.79; H, 4.69; N, 9.87; Cl, 12.71.

Similarly, using di(2-pyridyl)(p-methoxyphenyl)methanol and the same procedure yielded a white solid of melting point 91.5-92.5°. The mass spectrum of the product gave two peaks corresponding to m/e

296 and 294 of the parent molecular ion containing  $^{37}\text{Cl}$  and  $^{35}\text{Cl}$ , respectively. Anal. Calcd for  $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{O}$ : C, 73.34; H, 5.13; N, 9.50; Cl, 12.03. Found: C, 73.13; H, 4.90; N, 9.36; Cl, 12.27.

#### Synthesis of "Molecular" Silver

This element was prepared by internal electrolysis following the procedure of Gomberg.<sup>32</sup> Pure, well-washed silver chloride (100 g) was placed in a beaker and covered with water and a finely porous porcelain cell which contained water and several zinc bars, was placed upon the silver chloride. A piece of platinum sheet was put into the silver chloride and the zinc bars and platinum sheet were connected by a wire. Several drops of concentrated hydrochloric acid was then added to the water in the cell allowing the initial rate of the reaction to increase substantially. The reduction was completed in about 2 days.

The gray, powdery silver was first washed with water, 6 M  $\text{NH}_3$ , then again with water and finally with ethanol and ether. After drying in vacuo over sulfuric acid, it was heated to  $150^\circ$  and finally forced through a 100-mesh sieve. The product is more reactive than the less finely-divided, commercially available "silver powder."

#### Synthesis of Tetrakis(triphenylphosphine)platinum(0)

This compound was prepared according to the procedure<sup>35</sup> of R. Ugo, Cariati and La Monica except that the preparation was carried out under nitrogen. Triphenylphosphine (15.4 g 0.0588 mole) was dissolved in 200 ml of absolute ethanol and the solution heated to  $65^\circ$ . Potassium hydroxide (1.4 g) in 32 ml ethanol and 8 ml water was then added. Then 5.24 g (0.0126 mole) of potassium tetrachloroplatinate(II) dissolved in 50 ml of water was added dropwise to the

alkaline triphenylphosphine while stirring at 65°. Addition was completed in 20 minutes. After cooling, the yellow compound which precipitated during the addition was recovered by filtration under nitrogen, washed with 150 ml of warm ethanol, then with 60 ml of cold water and again with 50 ml of cold ethanol. The resulting yellow powder was dried in vacuo at room temperature for 2 hours. The yield was 12.5 g (80%).

#### Synthesis of Cis-diiodobis(triphenylphosphine)platinum(II)

A modification of the method of Mastin<sup>36</sup> involving the metathesis reaction between cis-dichlorobis(triphenylphosphine)platinum(II) and sodium iodide was employed. A mixture of 0.34 g of cis-dichlorobis-(triphenylphosphine)platinum(II) and 2.6 g of sodium iodide (1:40 mole ratio) in 40 ml of a solvent mixture containing equal volumes of chloroform, acetone, ethanol and water was refluxed for 4 hours. After separating from the aqueous layer, the bright yellow organic layer was evaporated to dryness. The bright yellow powder was then washed with water, benzene and finally with ethanol to give 0.43 g (90%) of product, mp 307-309° (lit<sup>37</sup> mp 303-304°). The ir spectrum in the 650-350 cm<sup>-1</sup> region showed 4 strong absorptions characteristic of the cis-isomer and compared to only 3 for the trans-isomer. On refluxing a chloroform solution of this cis-isomer, the orange trans-isomer (identical to the product from the reaction of tetrakis(triphenylphosphine)-platinum(0) with iodine) is obtained. The cis-trans isomerization can also be effected merely by heating the solid cis-isomer at 200°.

### Synthesis of Dichlorobis[4-pyridylbis(p-methoxyphenyl)methyl chloride]-Pd(II)

A suspension of  $\text{PdCl}_2\text{L}_2$  (1.7 g), where  $\text{L} = 4\text{-pyridylbis(p-methoxyphenyl)methanol}$ , in 10 ml of carbon tetrachloride was brought to a reflux and 5 ml of redistilled thionyl chloride was added. After 1/2 hour, during which all the solid went into solution, the solvent was evaporated off under reduced pressure whereupon a yellow solid precipitated out. The yellow solid was recrystallized twice in methylene chloride-hexane to yield 0.6 g (35%) of the product; mp 118-121°. Anal. Calcd for  $\text{C}_{38}\text{H}_{36}\text{Cl}_4\text{N}_2\text{O}_4\text{Pd}$ : Cl, 16.55. Found: Cl, 16.60.

Similarly,  $\text{PdCl}_2\text{L}_2$  where  $\text{L} = 4\text{-pyridyldiphenylmethyl chloride}$  or  $4\text{-pyridyldi(p-tolyl)methyl chloride}$  were prepared. Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{Cl}_4\text{N}_2\text{Pd}$ : C, 58.67; H, 3.83; N, 3.80, Cl, 19.24. Found: C, 58.67; H, 3.80; N, 3.78; Cl, 18.96. Anal. Calcd for  $\text{C}_{38}\text{H}_{36}\text{Cl}_4\text{N}_2\text{Pd}$ : C, 59.84; H, 3.96; N, 3.67; Cl, 18.59. Found: C, 59.87; H, 4.55; N, 3.88; Cl, 18.43.

### Reaction of Tetrakis(triphenylphosphine)platinum(0) With Iodine Monochloride

A solution of 0.50 g of tetrakis(triphenylphosphine)platinum(0) in 15 ml of benzene was mixed under nitrogen with a solution of 0.39 g of iodine monochloride (1:6 mole ratio) in 10 ml of ether. The mixture was then shaken for 5 minutes during which the color of the solution became rather dark and a nearly black solid began to form on the surface of the flask. Methanol (70 ml) was then added and the solution was shaken for 5 minutes during which the color of the solution became reddish brown with the settling down of a fine yellow precipitate. After standing for 5 minutes, the yellow precipitate was separated by



filtration and washed with methanol. The yield was 0.305 g (95%) of trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, mp 312° dec (lit<sup>36</sup> 310-314°). The ir spectrum of the product was identical to that of an authentic sample of trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and showed an absorption at  $\bar{\nu}_{\max}$  340 cm<sup>-1</sup> indicative of the Cl-Pt-Cl asymmetric stretch (lit<sup>37</sup> 342 cm<sup>-1</sup>). Recrystallization from benzene gave finally 0.240 g (74%) of lemon-yellow crystals.

Anal. Calcd for C<sub>36</sub>H<sub>30</sub>Cl<sub>2</sub>Pt: Cl, 8.97. Found: Cl, 8.88.

Similarly, by following the above procedure, the reaction of 0.50 g of Pt(PPh<sub>3</sub>)<sub>4</sub> and 0.195 g of ICl (1:3 mole ratio) yielded a yellow solution and a yellow-orange precipitate. Recrystallization from chloroform-ethanol or from benzene resulted in 0.32 g (81%) of trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, mp 304-305° (lit<sup>36</sup> 307-308°). It was identified by elemental analysis and by its ir spectrum. Anal. Calcd for C<sub>36</sub>H<sub>30</sub>I<sub>2</sub>Pt: I, 26.05. Found: I, 26.47.

The reaction was repeated for a third time using Pt(PPh<sub>3</sub>)<sub>4</sub> (1.0 g) and ICl (0.18 g) in a 1:1.1 mole ratio. The yield of a yellow solid, sparingly soluble in benzene, was 0.34 g. A small quantity (50 mg) of trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was also isolated by extracting the precipitate with 50 ml of hot benzene. The ir spectrum of the yellow solid indicated that Pt(II) complex had a cis-configuration, and the formula cis-PtClI(PPh<sub>3</sub>)<sub>2</sub> was assigned to it. The elemental analysis was consistent with this complex formula, but contaminated with PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. However, when this yellow solid was reacted with ICl in a 1:2.5 mole ratio, cis-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was isolated in 89% yield. This observation lends further support to the assigned formula, cis-PtClI(PPh<sub>3</sub>)<sub>2</sub>, for the yellow solid.

Reaction of *Trans*-diiodobis(triphenylphosphine)platinum(II) With Iodine Monochloride

To a chloroform solution containing 269 mg of *trans*-diiodobis-(triphenylphosphine)platinum(II) was added an ethereal solution containing 300 mg of iodine monochloride (1:6 mole ratio). The mixture was shaken for 10 minutes during which the solution turned dark violet in color. On adding 75 ml of methanol, a yellow solid precipitated out from the brownish-orange solution. After filtration, the solid was washed with methanol yielding 185 mg (77%) of *trans*-dichlorobis-(triphenylphosphine)platinum(II), identified by its ir spectrum and by elemental analysis. The yellow product dissolved completely in benzene and was recrystallized in this solvent, mp 308-311°. Anal. Calcd for  $C_{36}H_{30}Cl_2Pt$ : Cl, 8.87, Found: Cl, 9.18.

Reaction of *Trans*-dibromobis(triphenylphosphine)platinum(II) With Iodine Monochloride

The reaction of 100 mg of *trans*-dibromobis(triphenylphosphine)-platinum(II) with 45 mg of iodine monochloride (1:2.2 mole ratio) yielded, after the usual work-up, 74 mg of *trans*- $PtCl_2(PPh_3)_2$  (84%), mp 309-311°. Analysis of the sample obtained after recrystallization from benzene gave the following results: Calcd for  $C_{36}H_{30}Cl_2Pt$ : C, 54.69; H, 3.82; Cl, 8.97. Found: C, 54.05; H, 3.94, Cl, 8.93.

Reaction of *Cis*-chloriodobis(triphenylphosphine)platinum(II) With Iodine Monochloride

A mixture (1:2.5 mole ratio) of  $PtClI(PPh_3)_2$  (43 mg) dissolved in 10 ml  $CH_2Cl_2$  and  $ICl$  (20 mg) dissolved in 2 ml ether was stirred for 5 minutes. The solution was reduced, under reduced pressure, to 1/2 of its original volume and, after addition of 30 ml of ether,

white crystals of cis-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> precipitated out. The product was identified by its ir spectrum. Recrystallization from chloroform-ether yielded the pure product (32 mg, 89%).

Reaction of Cis-diiodobis(triphenylphosphine)platinum(II) With Iodine Monochloride

A 20 ml solution of CH<sub>2</sub>Cl<sub>2</sub> containing 70 mg cis-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was mixed with 2 ml of an ethereal solution containing 36 mg ICl (1:2.5 mole ratio). After stirring for 5 minutes, the solvent was concentrated to 2 ml by a stream of nitrogen. On addition of 25 ml of ether and 25 ml of ethanol, a white precipitate settled out and was separated by filtration, washed with ethanol and then with ether. The yield of cis-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was 55 mg (96%); and the product was identified by melting point (305°) and by its ir spectrum.

Reaction of Tetrakis(triphenylphosphine)platinum(0) With Iodine Monobromide

The same procedure for the reaction of Pt(PPh<sub>3</sub>)<sub>4</sub> with ICl was followed. The reaction of 0.50 g of the Pt(PPh<sub>3</sub>)<sub>4</sub> with 0.50 g of iodine bromide (1:6 mole ratio) afforded 0.360 g of yellow trans-dibromobis(triphenylphosphine)platinum(II) having a melting point of 312-314° (lit<sup>36</sup> 312-314°). On recrystallization from chloroform-ethanol, 0.311 g (86%) of the product was obtained. Anal. Calcd for C<sub>36</sub>H<sub>30</sub>Br<sub>2</sub>Pt: C, 49.16; H, 3.44; Br, 18.17. Found: C, 48.75; H, 3.39; Br, 17.99.

By using a 1:1 mole ratio, the reaction for 5 minutes of Pt(PPh<sub>3</sub>)<sub>4</sub> (0.93 g) with iodine monobromide (0.163 g) in benzene solution caused the precipitation of 0.48 g of a yellow precipitate.

After washing with EtOH, the solid was heated with 70 ml of benzene and the insoluble portion of the solid was then recrystallized from methylene chloride-benzene to give 0.20 g (30%) of cis-bromoiodobis-(triphenylphosphine)platinum(II) having a melting point of 308-309°. The cis-isomer was deduced from the ir spectrum. Also isolated was 70 mg of trans-diiodobis(triphenylphosphine)platinum(II). Anal. Calcd for  $C_{36}H_{30}BrIPt$ : Br, 8.63; I, 13.70. Found: Br, 8.47; I, 13.59.

The stoichiometric amounts of the reactants were further varied by using 1:2 and 1:3 mole ratios of  $Pt(PPh_3)_4$  to IBr. In each case a mixture of cis- $PtBrI(PPh_3)_2$  and trans- $PtI_2(PPh_3)_2$  were obtained. In the 1:2 reaction, approximately equivalent amounts of each product were isolated, whereas in the 1:3 reaction, 40% of cis- $PtBrI(PPh_3)_2$  and 60% of trans- $PtI_2(PPh_3)_2$  were obtained.

#### Reaction of Trans-diiodobis(triphenylphosphine)platinum(II) with Iodine Monobromide

A benzene solution containing 100 mg of trans-diiodobis(triphenylphosphine)platinum(II) and an ethereal solution containing 50 mg of iodine monobromide (1:2 mole ratio) was shaken for 10 minutes. Addition of 50 ml of methanol caused the precipitation of 71 mg of a yellow precipitate of trans-dibromobis(triphenylphosphine)platinum(II) (79%), melting point, 313-315°. After recrystallization from benzene, the sample was sent for analysis. Anal. Calcd for  $C_{36}H_{30}Br_2Pt$ : Br, 18.17. Found: Br, 17.86.

#### Reaction of Cis-bromoiodobis(triphenylphosphine)platinum(II) with Iodine Monobromide

To 50 mg of cis-bromoiodobis(triphenylphosphine)platinum(II)

dissolved in 10 ml of methylene chloride was added an ethereal solution containing 25 mg of iodine monobromide (1:2.2 mole ratio). After shaking the mixture for 5 minutes, the solution was concentrated to one-half the original volume under reduced pressure. On addition of 35 ml of methanol, 39 mg (84%) of cis-dibromobis(triphenylphosphine)-platinum(II) precipitated out, and was identified by its ir spectrum.

Reaction of Cis-diiodobis(triphenylphosphine)platinum(II) with Iodine Monobromide

A methylene chloride solution containing 60 mg of cis-diiodobis-(triphenylphosphine)platinum(II) was mixed with 2 ml of an ethereal solution containing 30 mg of iodine bromide. The mixture was stirred for 5 minutes after which the volume of the solution was reduced to about 3 ml by a stream of nitrogen. On addition of 40 ml of methanol, a pale yellow powder (45 mg, 83%) precipitated out, which was subsequently recrystallized from chloroform-methanol, melting point, 307-309° and identified by ir spectroscopy as cis-dibromobis(triphenylphosphine)platinum(II).

Reaction of Trans-diiodobis(triphenylphosphine)platinum(II) with Bromine

Trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (150 mg) was dissolved in a minimum amount of benzene and an ethereal solution containing 48 mg of bromine was then added to it. The mixture was stirred for 10 minutes after which methanol (50 ml) was added to it to cause the precipitation of trans-PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.130 mg, 96%). The product was removed by filtration, washed with methanol and ether, and subsequently recrystallized from benzene.

### Reaction of Tetrakis(triphenylphosphine)platinum(0) with Iodine

The reaction of tetrakis(triphenylphosphine)platinim(0) (0.50 g, 0.4 mmole) dissolved in 20 ml of benzene, and 0.30 g (1.2 mmole) of iodine produced a pale orange precipitate. After 10 minutes, 40 ml of methanol was added and on standing a further 10 minutes, filtering, and washing with methanol, 0.41 g (86%) of an orange precipitate was collected. Recrystallization from chloroform-methanol gave a bright orange precipitate, melting point, 314-315°. Heating the solid in vacuo at 100° resulted in loss of solvated chloroform. This compound is also soluble in benzene and its ir spectrum is identical to that of an authentic sample of trans-diiodobis(triphenylphosphine)platinum(II) in the 650-350  $\text{cm}^{-1}$  region<sup>36</sup>.

Reaction of a suspension of tetrakis(triphenylphosphine)platinum(0) in ethanol with iodine according to the method of Tayim and Ak1<sup>29</sup> also gave the same product, even though these authors did not specify which isomer was obtained.

### Reaction of Tetrakis(triphenylphosphine)platinum(0) with Bromine

A 1:4 mole ratio of  $\text{Pt}(\text{PPh}_3)_4$  to  $\text{Br}_2$  was used.  $\text{Pt}(\text{PPh}_3)_4$  (0.529 g) was dissolved in 15 ml of benzene and an ethereal solution containing 0.256 g of  $\text{Br}_2$  was added to this solution. The mixture was stirred for 3 minutes after which 30 ml of MeOH was added to cause more complete precipitation of the product, trans- $\text{PtBr}_2(\text{PPh}_3)_2$  (0.371 g, 98%). The ir spectrum of the precipitated product, which was identical to that of an authentic sample, did not indicate the presence of any cis-isomer. Recrystallization from benzene eventually yielded 0.240 g

(65%) of the pure product. Anal. Calcd for  $C_{36}H_{30}Br_2Pt$ : C, 49.16; H, 3.44; Br, 18.17. Found: C, 48.94; H, 3.36; Br, 17.96.

#### Reaction of Tetrakis(triphenylphosphine)platinum(0) with Chlorine

Chlorine gas was bubbled for 2 minutes through 3 ml of benzene. The yellow solution was then stirred and 15 ml of a benzene solution containing 0.50 g of  $Pt(PPh_3)_4$  was added in a fast dropwise fashion. After 1.0 minute, 50 ml of MeOH was added to the mixture to precipitate the product, trans- $PtCl_2(PPh_3)_2$ . No cis-isomer could be detected from an ir spectrum of the product which was recrystallized from benzene (yield: 70%). Anal. Calcd for  $C_{36}H_{30}Cl_2Pt$ : C, 54.62; H, 3.82; Cl, 8.97. Found: C, 54.58; H, 3.85; Cl, 8.84.

#### Reaction of Tetrakis(triphenylphosphine)platinum(0) with Diphenylmethyl Bromide

Tetrakis(triphenylphosphine)platinum(0) (0.5 g, 0.40 mmole) in 20 ml of benzene was mixed with a benzene solution containing 0.20 g (0.85 mmole) of diphenylmethyl bromide, the yellow Pt(0) complex solution was decolorized and on standing for 1/2-3/4 hour, the pale yellow solid was filtered off to give 0.31 g (38%) of cis-dibromobis-(triphenylphosphine)platinum(II), melting point, 307-308°. No esr signal could be detected from the reaction mixture and work-up of the mother liquor yielded 80 mg of sym-tetraphenylethane having a melting point of 209-211° (lit<sup>38</sup> 208-210°)

#### Reaction of Tetrakis(triphenylphosphine)platinum(0) with Triphenylmethyl Bromide and Triphenylmethyl Chloride

The reaction between 0.95 g (0.79 mmole) of tetrakis(triphenylphosphine)platinum(0) dissolved in 20 ml of benzene and a 10 ml solution

of benzene containing 0.40 g (1.24 mmole) of triphenylmethyl bromide afforded, after 1/2 hour, 0.54 g (80%) of crystals of cis-dibromobis-(triphenylphosphine)platinum(II). The solution gave a very intense but poorly resolved esr signal; however, the resolution was much improved when the radical concentration was diluted. Examination of the esr spectrum showed it to be the triphenylmethyl by comparison with the literature spectrum<sup>39</sup>. The radical was also characterized as ditritylperoxide, identified by its melting point, 178-180° (lit<sup>40</sup> 178-179°) and by comparison with the ir spectrum<sup>40</sup> of an authentic sample of ditritylperoxide.

In a similar procedure, the reaction of the Pt(0) complex with triphenylmethyl chloride for 5 minutes was shown to yield cis-dichlorobis(triphenylphosphine)platinum(II) (43%) and triphenylmethyl radicals.

#### Reaction of Tetrakis(triphenylphosphine)platinum(0) with 4-Pyridyldiphenylmethyl Chloride

Tetrakis(triphenylphosphine)platinum(0) (0.93 g) was dissolved in 15 ml of benzene and an equimolar amount of 4-pyridyldiphenylmethyl chloride (0.204 g) was added as a benzene solution. The yellow solution turned dark brown and a precipitate came down. On standing for 1/2 hour, the solid was filtered off to yield 2.30 g of cis-dichlorobis(triphenylphosphine)platinum(II), identified by its melting point of 305° and an infrared spectrum. The reaction mixture gave a strong esr signal, indicative of free-radicals.

When the mother liquor was evaporated to dryness in the dry box, a yellow gum resulted. This was then redissolved in some benzene,



adsorbed on alumina and eluted with benzene. The eluent from an intense yellow band was evaporated to dryness to give sticky, orange crystals; melting point, 200-230°. Mass spectrum analysis of this solid gave intense peaks at  $m/e = 488$  and  $244$ , consistent with the assignments  $C_{36}H_{28}N_2^+$  and  $C_{18}H_{14}N^+$  respectively.

Reaction of Chlorocarbonylbis(triphenylphosphine)iridium(I) with  
Trityl Bromide

Benzene solutions containing  $IrCl(CO)(PPh_3)_2$  (0.272 g) and  $Ph_3CBr$  (0.250 g) in a 1:2.2 mole ratio were mixed in the dry box and stirred. The yellow solution turned orange and after 5 minutes a sample of it was taken out of the dry box and examined by esr spectroscopy. A strong signal was obtained and the detected radical was identified as  $Ph_3C\cdot$ . The solution was concentrated to 10 ml under reduced pressure. After 3 hours of stirring, filtration of the reaction mixture yielded 0.270 g (80%) of a yellow precipitate, melting point, 304-308°. The product was recrystallized from an equivolume of  $CHCl_3$  and  $CH_2Cl_2$  (mp 310-312°) and was identified as  $IrBr_2Cl(CO)(PPh_3)_2$  by comparison of its ir spectrum with that of an authentic sample prepared by reaction of  $IrCl(CO)(PPh_3)_2$  with  $Br_2$ .<sup>41</sup>

Reaction of Chlorocarbonylbis(triphenylphosphine)iridium(I) with  
Diphenylmethyl Bromide

Chlorocarbonylbis(triphenylphosphine)iridium(I) (0.270 g) was dissolved in 50 ml of benzene and 0.191 g of  $Ph_2CHBr$  was added to the solution. The mixture was stirred and after 16 hours the yellow precipitate (0.262 g), identified by ir spectroscopy as  $IrBr_2Cl(CO)(PPh_3)_2$ , was removed by filtration. The filtrate was then concentrated under reduced pressure to a small volume (2 ml). Addition of methanol (20 ml)

yielded more yellow solid (55 mg) which was filtered off. The total isolated product containing Ir was 0.310 g (95%). The mother liquor was then evaporated to dryness yielding colorless crystals of sym-tetraphenylethane (mp 208-210°).

Reaction of Chlorocarbonylbis(triphenylphosphine)iridium(I) with a Mixutre of Trityl and Diphenylmethyl Bromide

Equimolar quantities of the three reactants were used in this experiment. A benzene solution containing trityl and diphenylmethyl bromide (114 mg and 87 mg, respectively) was added to a benzene solution of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  (275 mg). The yellow solution turned orange and after several minutes the yellow color returned. After 2 hours, the reaction mixture was examined by esr spectroscopy. No radicals, however, could be detected. The reaction was stirred overnight and the precipitated product (0.299 g, 90%)  $\text{IrBr}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , was removed by filtration. The solvent was then removed from the mother liquor to give 169 mg of pale yellow solid which was dissolved in a minumum amount of cyclohexane. This solution was then filtered, and a little petroleum ether was then added and the solution allowed to stand on a cold plate whereupon pentaphenylethane precipitated out, mp 168-180° (lit<sup>42</sup> 168-184°). Mass spectrum analysis of this compound showed intense peaks corresponding to m/e of 243 and 167, corresponding to  $\text{Ph}_3\text{C}^+$  and  $\text{Ph}_2\text{CH}^+$ , respectively. Weak peaks at m/e 410 and 333 assigned to the molecular ion and  $\text{Ph}_4\text{C}_2\text{H}^+$  were also observed.

## RESULTS AND DISCUSSION

### Synthesis

The triarylmethyl chlorides, intended precursors in the generation of the corresponding triarylmethyl radicals, were prepared from the corresponding methanols by chlorination with either hydrogen chloride or thionyl chloride. In each case, the nitrogen atom in the heterocyclic ring is protonated and the major problem which had to be solved in the synthesis involved the deprotonation of the nitrogen atom which had to be done in non-aqueous medium since the triarylmethyl chlorides are sensitive to moisture. Initially, attempts were made to achieve deprotonation by sublimation in vacuo and in the presence of sodium hydroxide. This was undertaken with the expectation that the hydrochloride salt of the triarylmethyl chloride might dissociate into the triarylmethyl chloride and free hydrogen chloride during sublimation and that the hydrogen chloride would be absorbed by the sodium hydroxide before it could recombine with the free triarylmethyl chloride. This procedure proved to be unsuccessful. Eventually, the problem was solved elegantly by employing 2,6-lutidine, a stronger base than the triarylmethyl chlorides. The general procedure involved dissolving the hydrochloride salt in a minimum of methylene chloride and subsequent addition of a 3- to 5-fold excess of 2,6-lutidine to the solutions until precipitation of lutidinium chloride occurred. A non-polar solvent, such as benzene, was used to effect more complete precipitation

of lutidinium chloride. Filtration and subsequent evaporation of volatile, filtrate components of all solvents yielded the desired product. The triarylmethyl chlorides, all soluble in benzene or n-hexane, either can be recrystallized from these solvents or sublimed in vacuo to yield a pure product. In some instances, sublimation of the impure product containing colored impurities led to decomposition of the products as evidenced by the formation of more colored decomposition products. The colored impurities also seem to lead to the formation of oils in the recrystallization process. However, it was found that treatment with animal charcoal was effective in removal of most of these impurities; after their removal, a pure crystalline product could be obtained. The hydrochloride salt of 4-pyridyldi-(p-tolyl)methyl chloride contained a colored impurity which could not be removed either by treatment with animal charcoal or by recrystallization. However, with HCl gas used as the chlorinating agent, deprotonation of the resulting salt followed by recrystallization yielded the pure product without difficulty.

The palladium complexes of triarylmethyl halides were prepared from the corresponding complexed carbinols by reaction with thionyl chloride. The complex was usually suspended in a halocarbon such as  $\text{CCl}_4$  and, on addition of excess thionyl chloride, the complex dissolved. It is worthwhile to mention two observations. Firstly, the complex of 4-pyridyldiphenylcarbinol crystallizes out with solvent of recrystallization (methanol). If this solvent of recrystallization was removed by heating, the desolvated complex would not dissolve in thionyl chloride and chlorination could not be accomplished. Secondly, attempts to prepare 4-pyridylbis(p-methoxyphenyl)methyl chloride from the methanol

by chlorination with  $\text{HCl}$  or  $\text{SOCl}_2$  were unsuccessful because a reddish brown gum resulted each time. The complexed methanol, however, could be easily chlorinated. The ir spectra of some triarylmethyl chlorides and the palladium(II) complexes of three of these are shown in figures 1-7.

### Generation of Free-Radicals by Reaction of $\text{Pt}(0)$ With Triarylmethyl Halides

#### Visible Spectra

A benzene solution of triarylmethyl halide,  $\text{Ar}_3\text{CCl}$ , was syringed into a  $10^{-3}\text{M}$  benzene solution of  $\text{Pt}(\text{PPh}_3)_4$  contained in a serum-capped cuvette and the visible spectrum of the resulting mixture was monitored. The visible spectra of solutions resulting from the reaction of the  $\text{Pt}(0)$  complex with  $\text{Ph}_3\text{CCl}$ ,  $(p\text{-ClC}_6\text{H}_4)_3\text{CCl}$  and  $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{CCl}$ , respectively, showed the same absorptions as the solutions resulting from the reaction of the same triarylmethyl chlorides with "molecular" silver. The latter series of reactions typify the classical method of Gomberg for the generation of triarylmethyl radicals. Thus, the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with triarylmethyl halides must have produced the corresponding triarylmethyl radicals. This is further substantiated by the observation that the spectra of the reaction mixtures of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{Ph}_3\text{CCl}$  and with  $\text{Ph}_3\text{CBr}$  were observed to be identical and that the lowest energy absorption at 513 nm compares well with the literature value of 515 nm<sup>43</sup> for  $\text{Ph}_3\text{C}\cdot$ . The Pt-containing product from these reactions is cis-dihalogenobis(triphenylphosphine)platinum(II), which was identified by ir spectroscopy. The reaction of  $\text{Pt}(\text{PPh}_3)_4$  with these triarylmethyl halides forming cis-dihalogenobis(triphenylphosphine)-platinum(0) and triarylmethyl radicals (in equilibrium with their

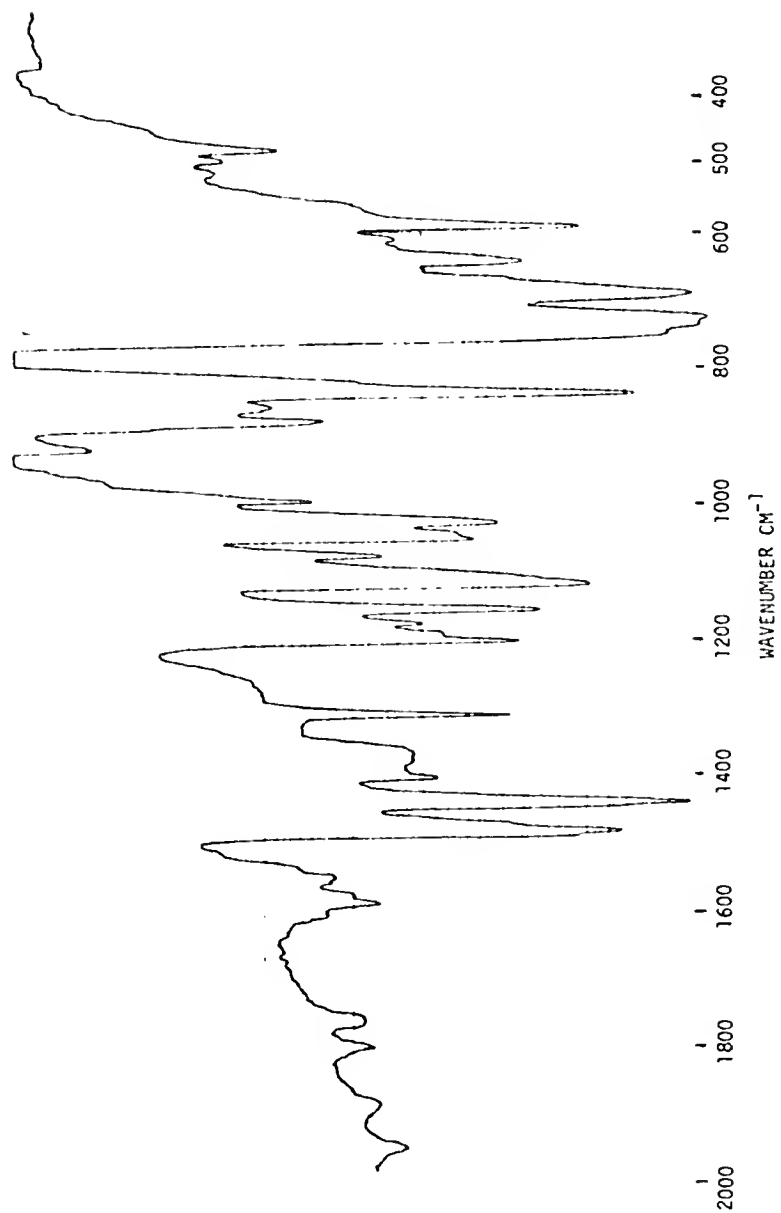


Figure 1. Infrared Spectrum of 2-thiazolyldiphenylmethyl Chloride

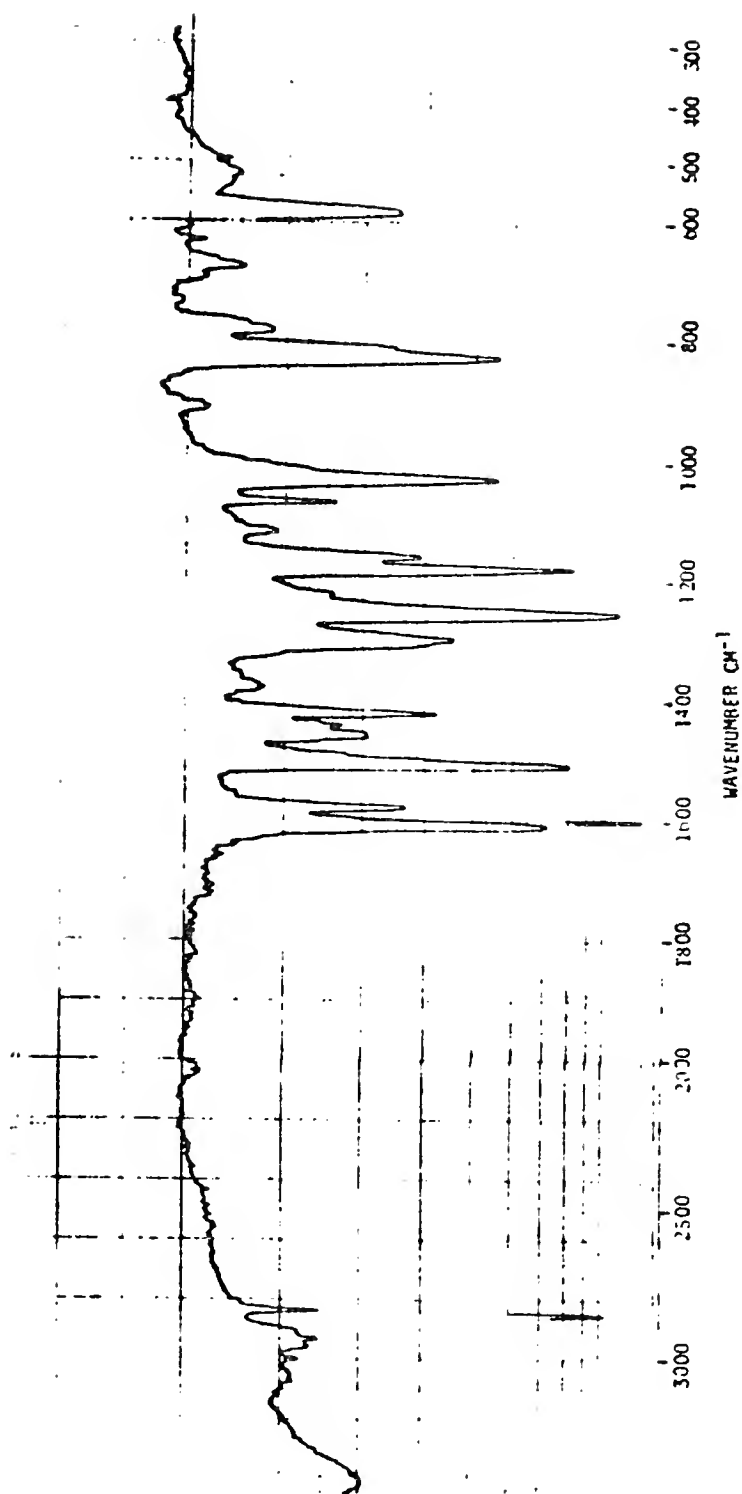


Figure 2. Infrared Spectrum of Di(2-pyridyl)(p-tolyl)methyl Chloride

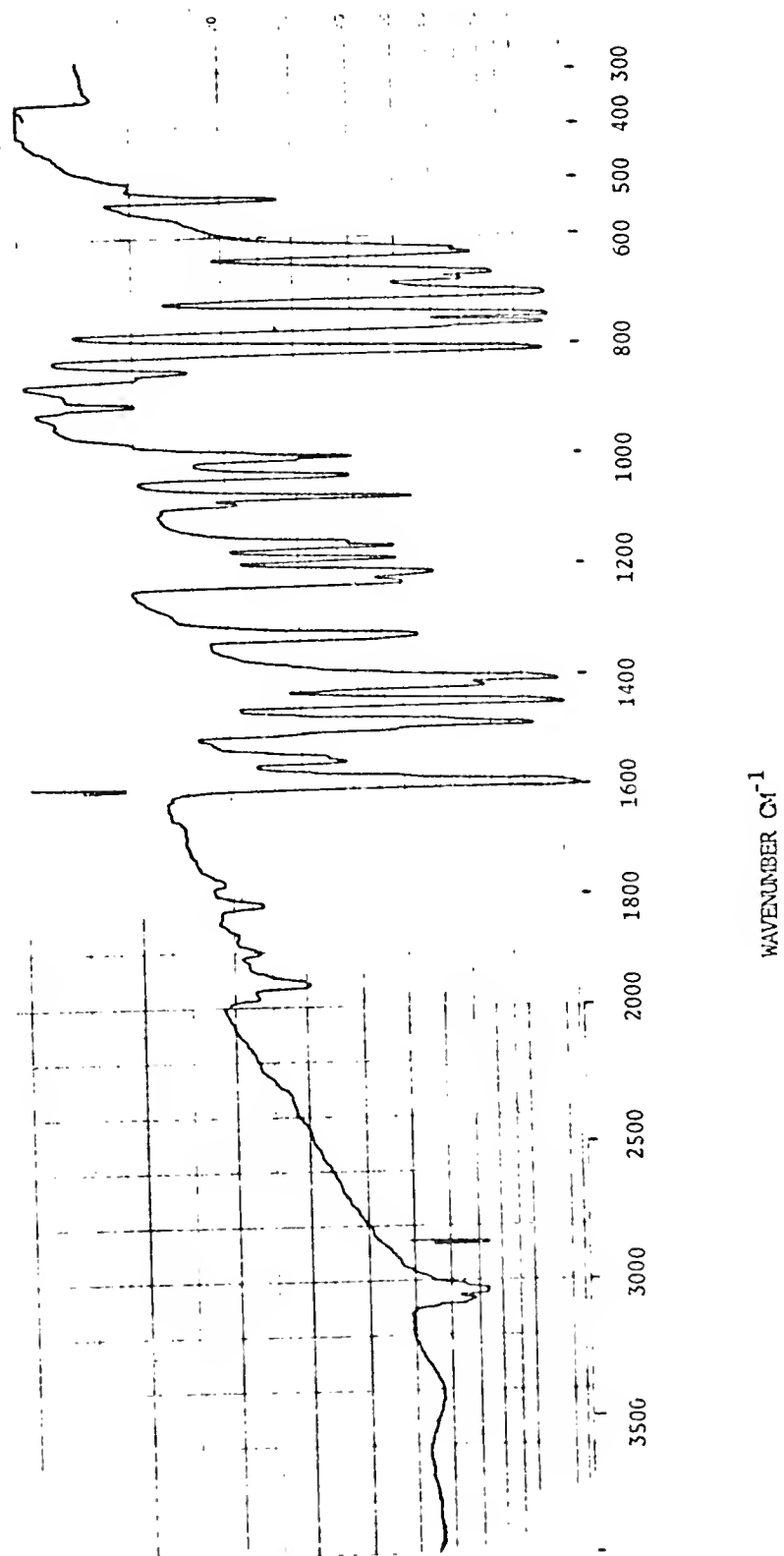


Figure 3. Infrared Spectrum of 4-pyridyldiphenylmethyl Chloride



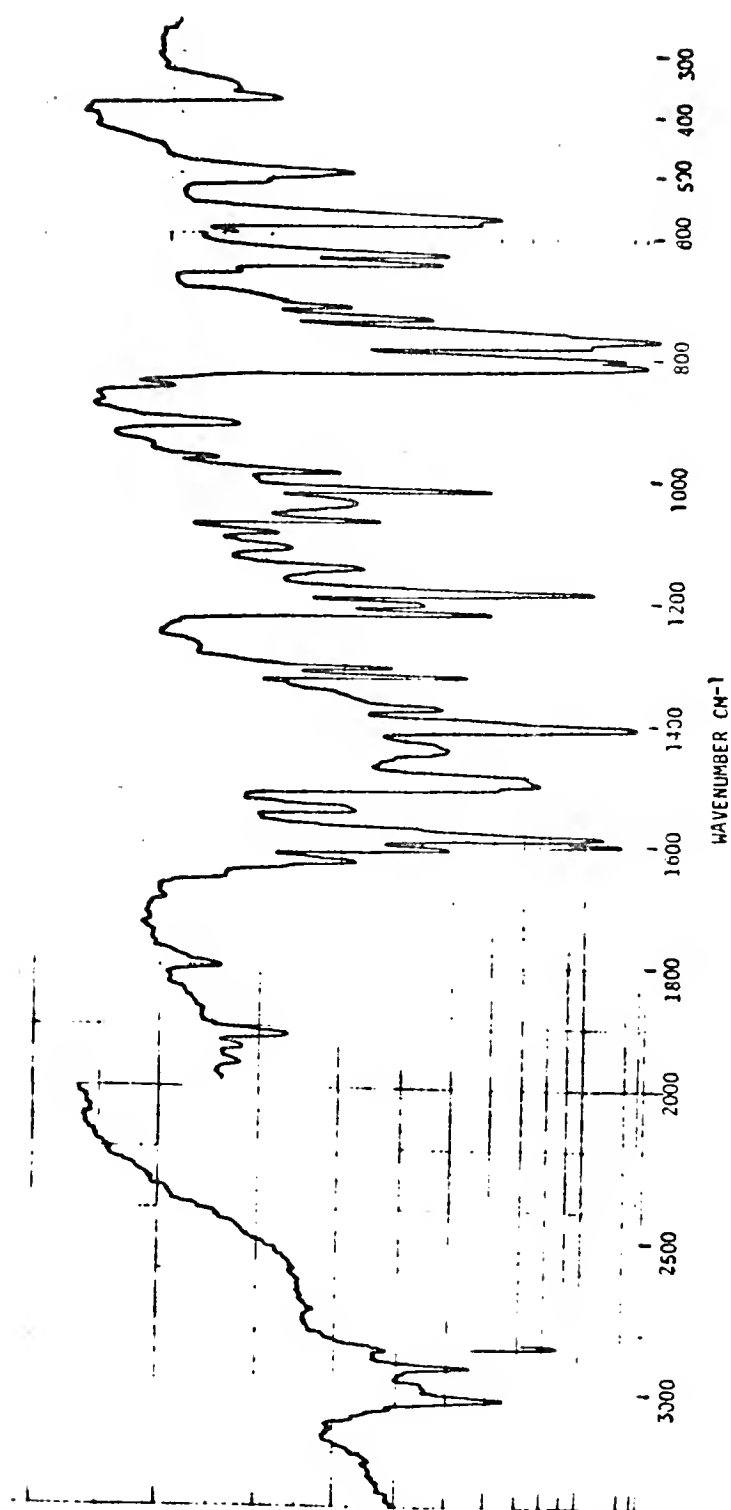


Figure 4. Infrared Spectrum of 4-pyridyldi(p-tolyl)methyl chloride

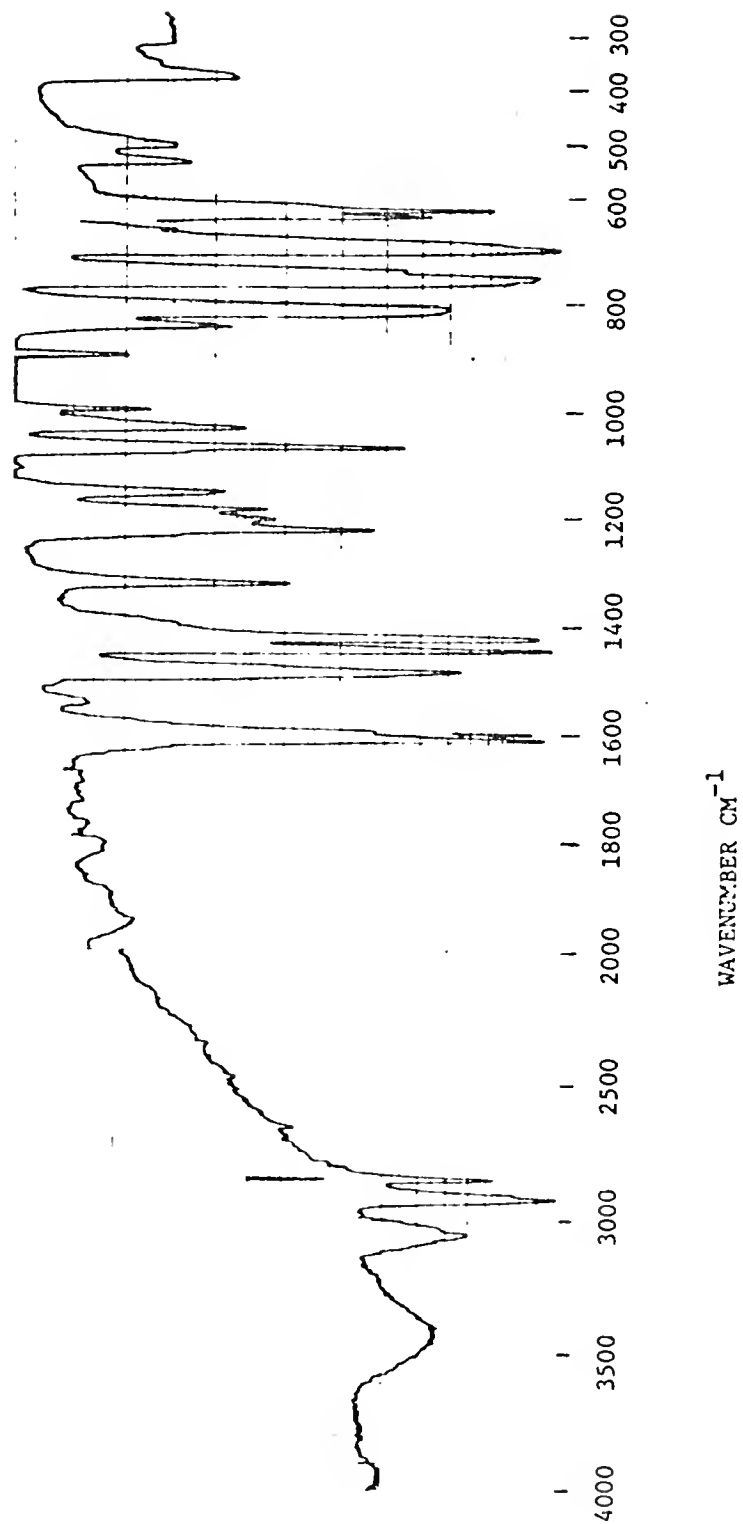


Figure 5. Infrared Spectrum of Dichlorobis(4-pyridyl)diphenylmethyl chloride palladium(II)

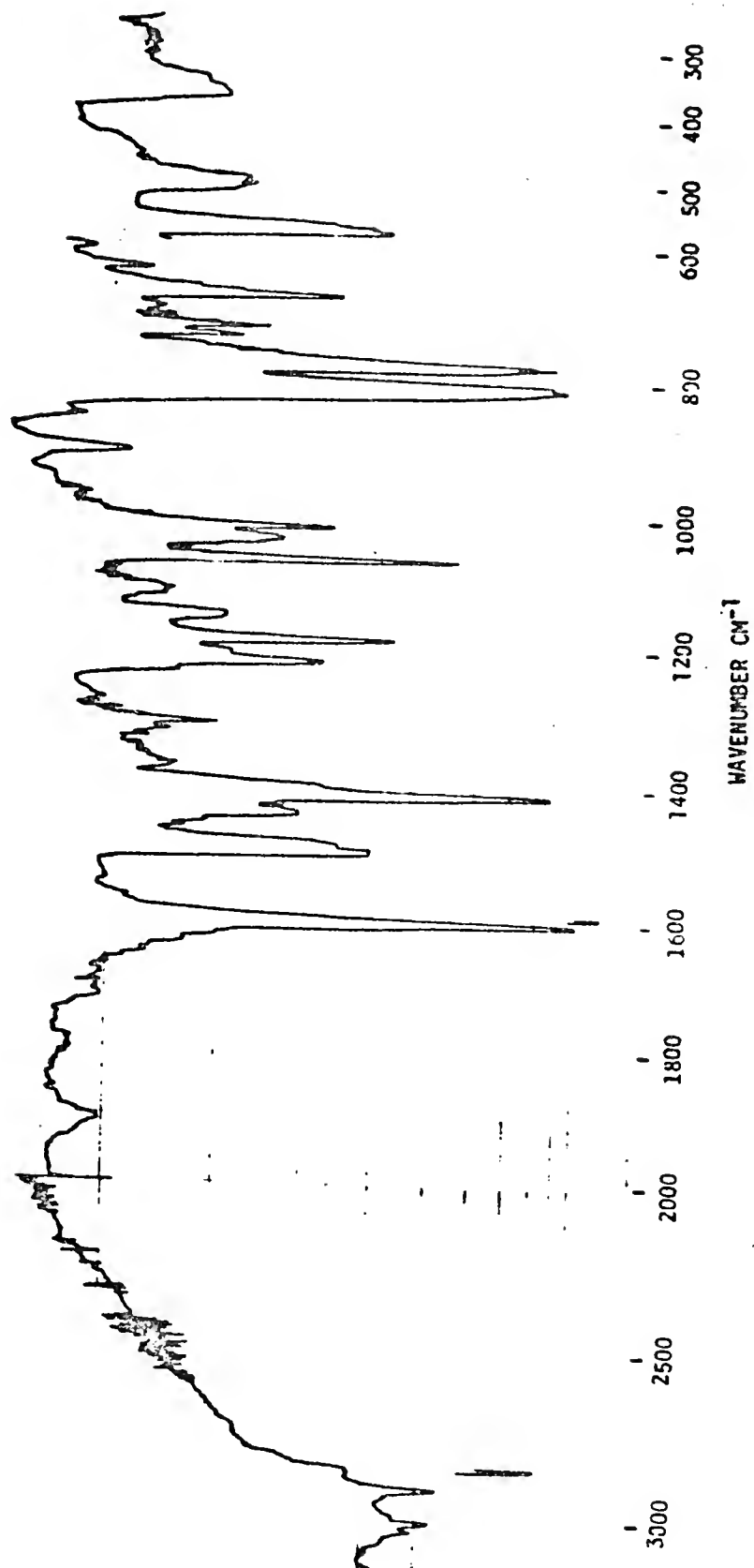


Figure 6. Infrared Spectrum of Dichlorobis[4-pyridyl]di(p-tolyl)methyl chloride palladium(II)

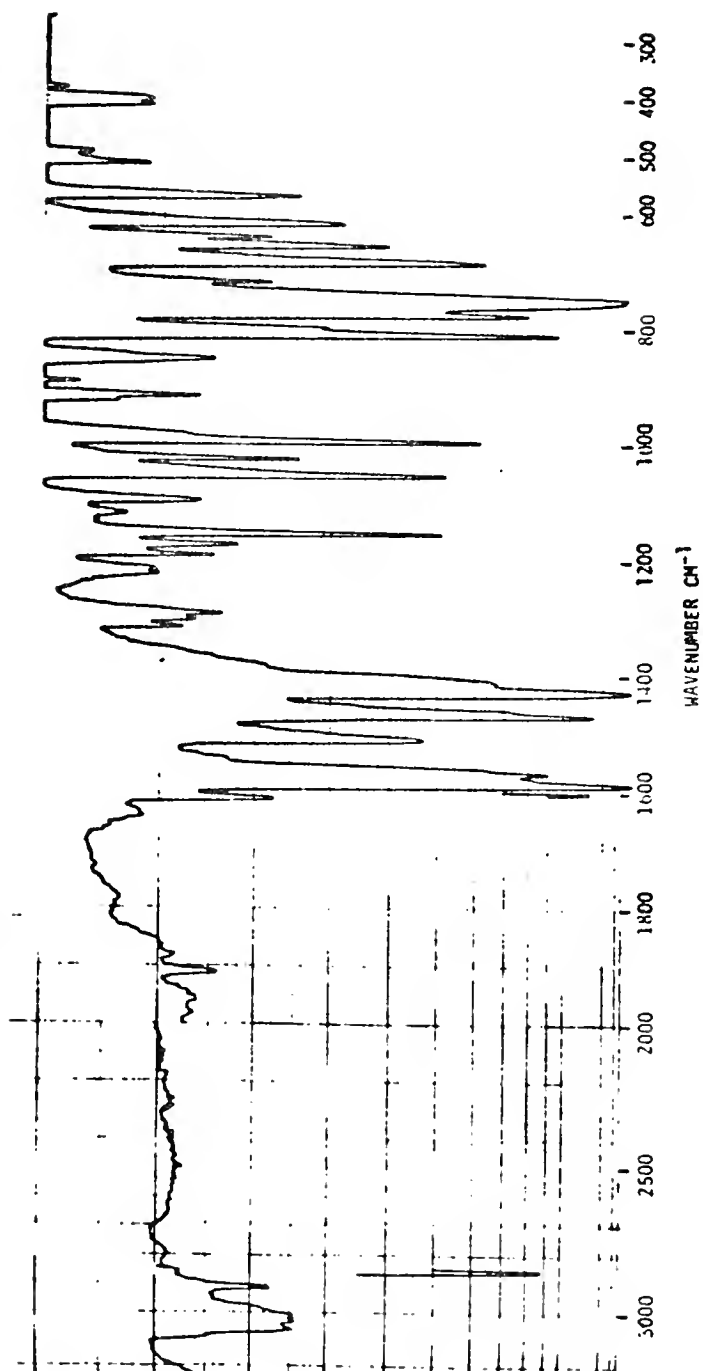


Figure 7. Infrared Spectrum of Dichlorobis[4-pyridylbis(p-methoxyphenyl)methyl chloride]palladium(II)

dimers), contrasts markedly with the classical oxidative addition of alkyl halides, e.g.,  $\text{CH}_3\text{I}$ , to  $\text{Pt}(\text{PPh}_3)_4$  forming trans- $\text{PtICH}_3(\text{PPh}_3)_2$ .

The report<sup>14</sup> that trityl bromide reacts with  $\text{Pt}(\text{PPh}_3)_4$  to yield  $\text{PtBr}(\text{Ph}_3\text{C})(\text{PPh}_3)_2$  was found to be in error.

When the triarylmethyl halides containing a heterocyclic ring such as 4-pyridyl were reacted with Ag, no characteristic absorption indicative of the formation of free-radicals was noted in the visible spectra. The same observations were made with 4-pyridyldiphenylmethyl, 4-pyridyldi(p-tolyl)methyl and 4-pyridylbis(p-methoxyphenyl)methyl chlorides coordinated to Pd(II). However, when these triarylmethyl halides, free or complexed with Pd(II), were reacted with  $\text{Pt}(\text{PPh}_3)_4$ , peaks in the 500 nm regions characteristic of free-radicals, appeared immediately. Thus, the formation of free-radicals from triarylmethyl halides is faster by using  $\text{Pt}(\text{PPh}_3)_4$  than with Ag. The visible spectral data of the various free-radicals and their mode of generation are tabulated in Table 1. The possibility that these peaks could be attributed to carbonium ions can be ruled out for the following reasons: (1) The visible spectrum of  $\text{Ph}_3\text{C}^+$  (generated from  $\text{Ph}_3\text{COH}$  and concentrated  $\text{H}_2\text{SO}_4$  or from a solution of  $\text{Ph}_3\text{CPF}_6$  in  $\text{CH}_2\text{Cl}_2$ ) shows two broad absorptions at  $\lambda_{\text{max}}$  404 and 431 nm compared to  $\lambda_{\text{max}}$  513, 485 and 475 nm for  $\text{Ph}_3\text{C}\cdot$ . Similarly, spectra of  $(\text{p-CH}_3\text{C}_6\text{H}_4)_3\text{C}^+$  and  $(\text{p-ClC}_6\text{H}_4)_3\text{C}^+$  show absorption peaks at 452 nm and 465 nm, respectively, whereas those for the corresponding radicals are at 526 nm and 533 nm, respectively. Thus, no carbonium ions are formed in the reaction of Pt(0) with triarylmethyl halides. (2) The presence of free-radicals in the solutions is demonstrated by esr spectroscopy which will be described in the next section.

TABLE 1  
 $\lambda_{\max}$  in the Visible Spectra of Triarylmethyl Radicals in Benzene

Halide	Reductant(s)	Radical	$\lambda_{\max}$
$\text{Ph}_3\text{CCl}$ , $\text{Ph}_3\text{CBr}$	$\text{Ag}$ , $\text{Pt}(\text{PPh}_3)_4$	$\text{Ph}_3\text{C}\cdot$	513, 485, 475
$(\underline{p}\text{-Cl-C}_6\text{H}_4)_3\text{CCl}$	$\text{Ag}$ , $\text{Pt}(\text{PPh}_3)_4$	$(\underline{p}\text{-Cl-C}_6\text{H}_4)_3\text{C}\cdot$	533, 504, 493
$(\underline{p}\text{-CH}_3\text{-C}_6\text{H}_4)_3\text{CCl}$	$\text{Ag}$ , $\text{Pt}(\text{PPh}_3)_4$	$(\underline{p}\text{-CH}_3\text{-C}_6\text{H}_4)_3\text{C}\cdot$	526, 498, 486
$(4\text{-C}_6\text{H}_4\text{N})\text{Ph}_2\text{CCl}$	$\text{Pt}(\text{PPh}_3)_4$	$(4\text{-C}_6\text{H}_4\text{N})\text{Ph}_2\text{C}\cdot$	501
$(4\text{-C}_6\text{H}_4\text{N})(\underline{p}\text{-CH}_3\text{-C}_6\text{H}_4)_2\text{CCl}$	$\text{Pt}(\text{PPh}_3)_4$ , $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	$(4\text{-C}_6\text{H}_4\text{N})(\underline{p}\text{-CH}_3\text{-C}_6\text{H}_4)_2\text{C}\cdot$	509
$\text{PdCl}_2\text{L}_2$ , $\text{L}=(4\text{-C}_6\text{H}_4\text{N})\text{Ph}_2\text{CCl}$	$\text{Pt}(\text{PPh}_3)_4$	a	520, 497
$\text{PdCl}_2\text{L}_2$ , $\text{L}=(4\text{-C}_6\text{H}_4\text{N})(\underline{p}\text{-CH}_3\text{-C}_6\text{H}_4)_2\text{CCl}$	$\text{Pt}(\text{PPh}_3)_4$	a	531
$\text{PdCl}_2\text{L}_2$ , $\text{L}=(4\text{-C}_6\text{H}_4\text{N})(\underline{p}\text{-MeO-C}_6\text{H}_4)_2\text{CCl}$	$\text{Pt}(\text{PPh}_3)_4$	a	542

<sup>a</sup> Radicals not identified.

Finally, the reaction mixture of the Pt(0) complex with chlorides containing two pyridyl rings or a thiazolyl ring did not show any absorption peaks around the 500 nm region characteristic of free-radicals even though the yellow color of the Pt(0) complex turned orange when the two solutions were mixed. The reason is probably due to the great instability of the free-radicals formed.

### Esr Spectroscopy

Benzene solutions of the triarylmethyl radicals were usually generated by adding excess organic halide to  $10^{-3}$  -  $10^{-2}$ M Pt(PPh<sub>3</sub>)<sub>4</sub> and the resulting solution scanned at room temperature. For radicals which are unstable with respect to the corresponding dimers or disproportionation products and whose esr signals decreased rapidly with time, the spectra were run at 10°. No esr signal could be detected in mixtures of Pt(0) solutions and chloride solutions containing two pyridyl rings or a thiazoyl ring. It was found also that, for the case of 4-pyridyldi(p-tolyl)methyl chloride, an esr spectrum could be obtained by reaction with silver even though the visible spectrum did not indicate the formation of free-radicals. The esr signal strength did decrease significantly within a matter of minutes. These observations seem to reflect the fact that esr spectroscopy is a more sensitive method than visible spectroscopy and, hence, can detect the small concentration of free-radicals formed from the slow reaction of the chloride and silver. All the spectra are characterized by a g-value of 2.0 and by extensive hyperfine structure. The plethora of lines sometimes exceeded one hundred. Even so, this represents but a fraction of the total number of lines theoretically calculated to be 343 and 2025

for triphenylmethyl and 4-pyridyldiphenylmethyl radicals, respectively. Whenever a solution spectrum did not contain hyperfine structure, the solution was usually diluted to prevent "exchange narrowing," which has the effect of masking hyperfine structure by collapsing the esr signal into a single line. In some instances, better resolution was achieved by dilution. The esr spectra of  $\text{Ph}_3\text{C}\cdot$  and  $(p\text{-ClC}_6\text{H}_4)_3\text{C}\cdot$  are identical to published spectra of the same species<sup>44</sup>. The others are shown in figures 8-13. No attempt was made at interpretation of these complex spectra because it lies outside the scope of this work.

The reaction of triarylmethyl halides is faster with  $\text{Pt}(\text{PPh}_3)_4$  than with Ag. Whereas no advantage is gained by using the  $\text{Pt}(0)$  rather than Ag for generation of radicals from halides containing no heterocyclic rings, the use of  $\text{Pt}(0)$  is critical in the case of those halides containing heterocyclic rings or in complexed halides. In the former case, the presence of an electronegative nitrogen atom in the heterocyclic rings appears to lower the stability with respect to dimers or disproportionation products of the generated radicals. If the rate of generation of the radicals is slow as is the case when Ag is used, the rate of disproportionation, for example, may be comparable to it so that the concentration of free-radical is too low to be detected by visible spectroscopy. When a halide is complexed to a  $\text{Pd}(\text{II})$  atom, the results indicate that its reactivity with Ag is too slow to be of any utility in generating radicals, but by using  $\text{Pt}(0)$ , radicals, probably complexed radicals, are formed rapidly. Hence, the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with a triarylmethyl halide appears to be a superior method for the generation of free-radicals than Gomberg's method.



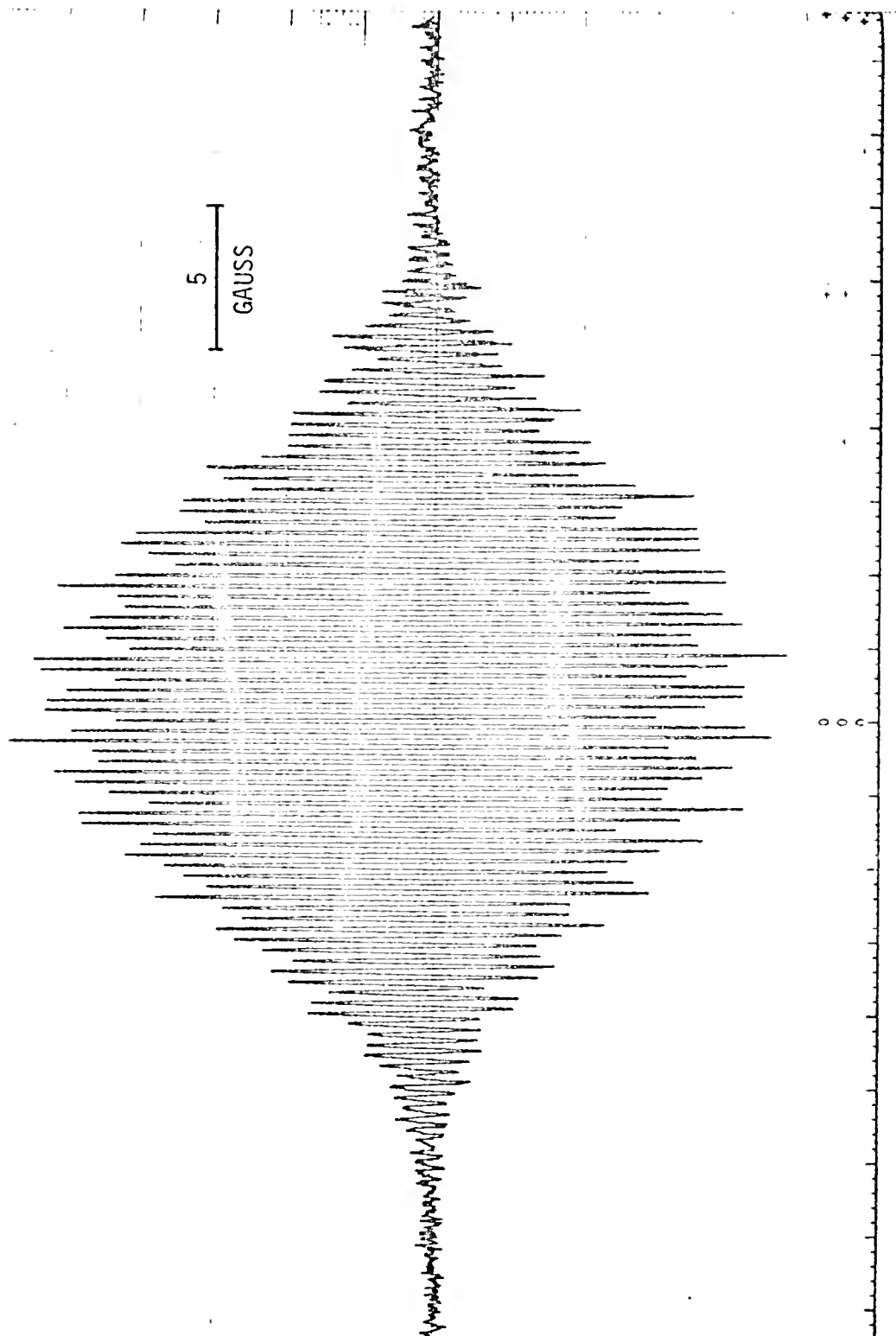


Figure 8. ESR Spectrum of Tri(p-tolyl)methyl Radical at 23°

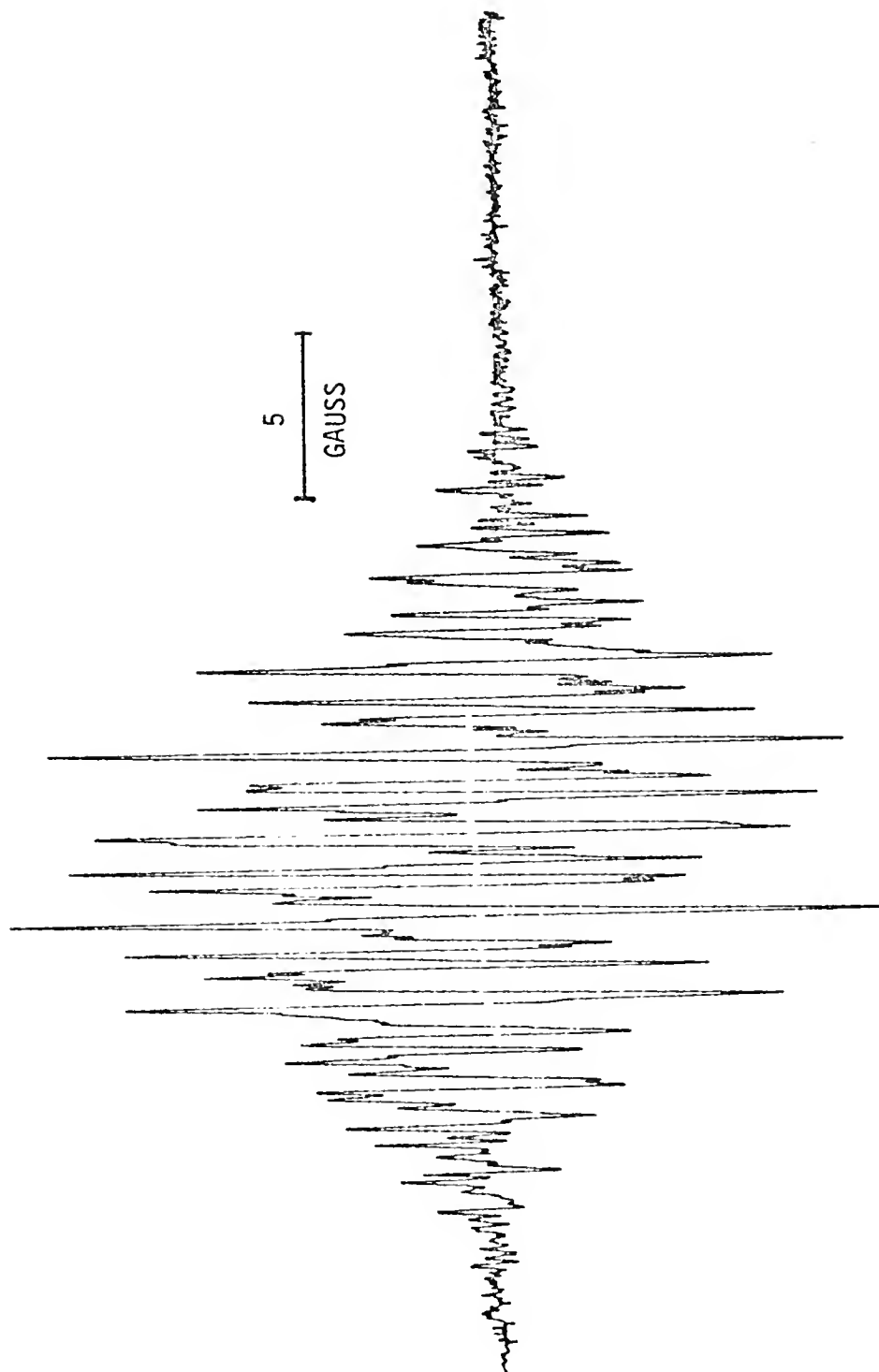


Figure 9. ESR Spectrum of 4-pyridyldiphenylmethyl Radical at 23°

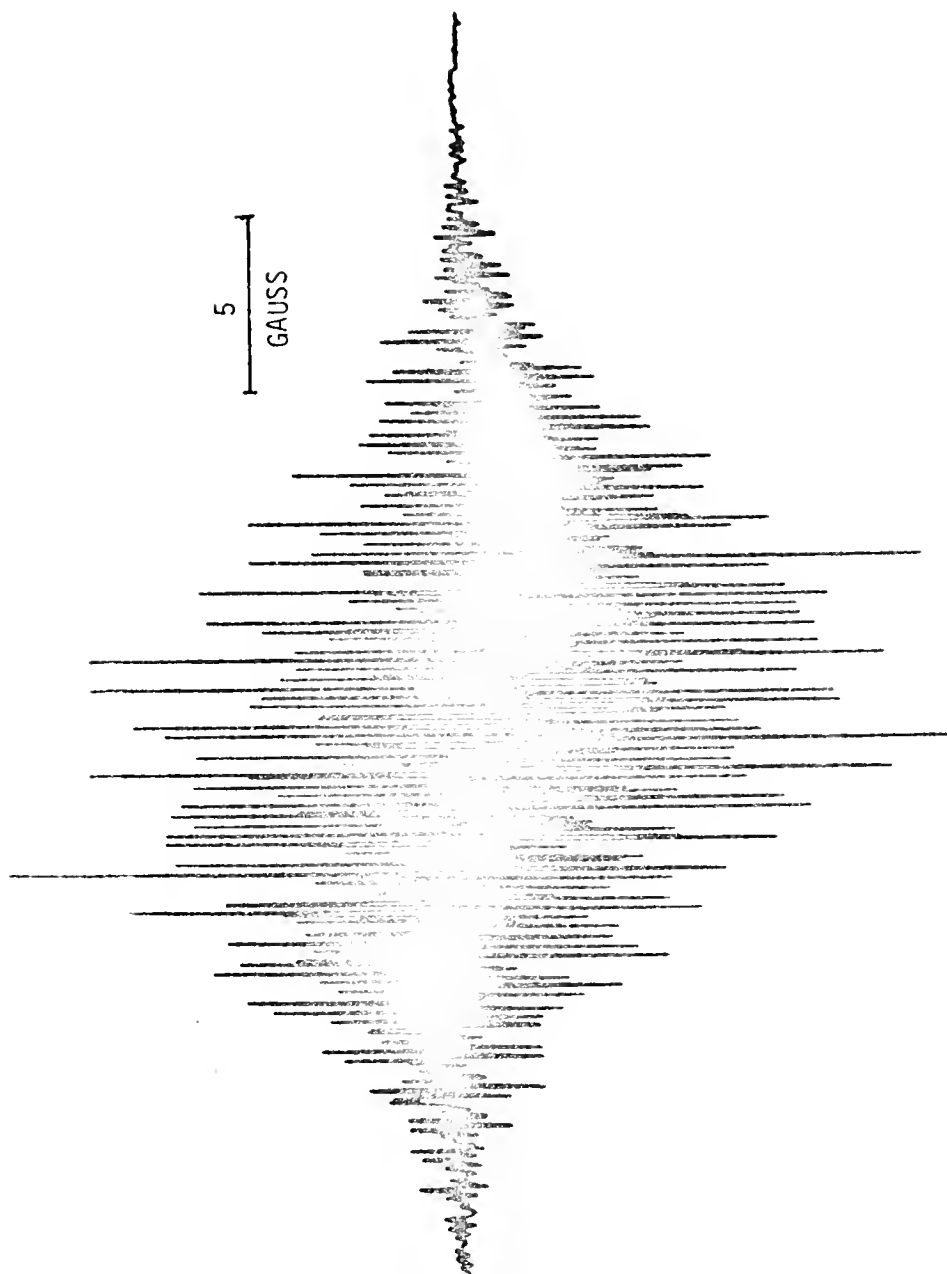


Figure 10. ESR Spectrum of 4-pyridyl di(p-tolyl)methyl Radical at 10°



Figure 11. ESR Spectrum of Radical Derived From the Reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{PdCl}_2\text{L}_2$ ,  $\text{L} = (\text{C}_5\text{H}_5\text{N})\text{Ph}_2\text{CCl}$ . Temp  $23^\circ$



Figure 12. ESR Spectrum of Radical Derived From the Reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{PdCl}_2\text{L}_2$ ,  $\text{L} = (\text{C}_5\text{H}_4\text{N})(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{CCl}$ . Temp  $23^\circ$

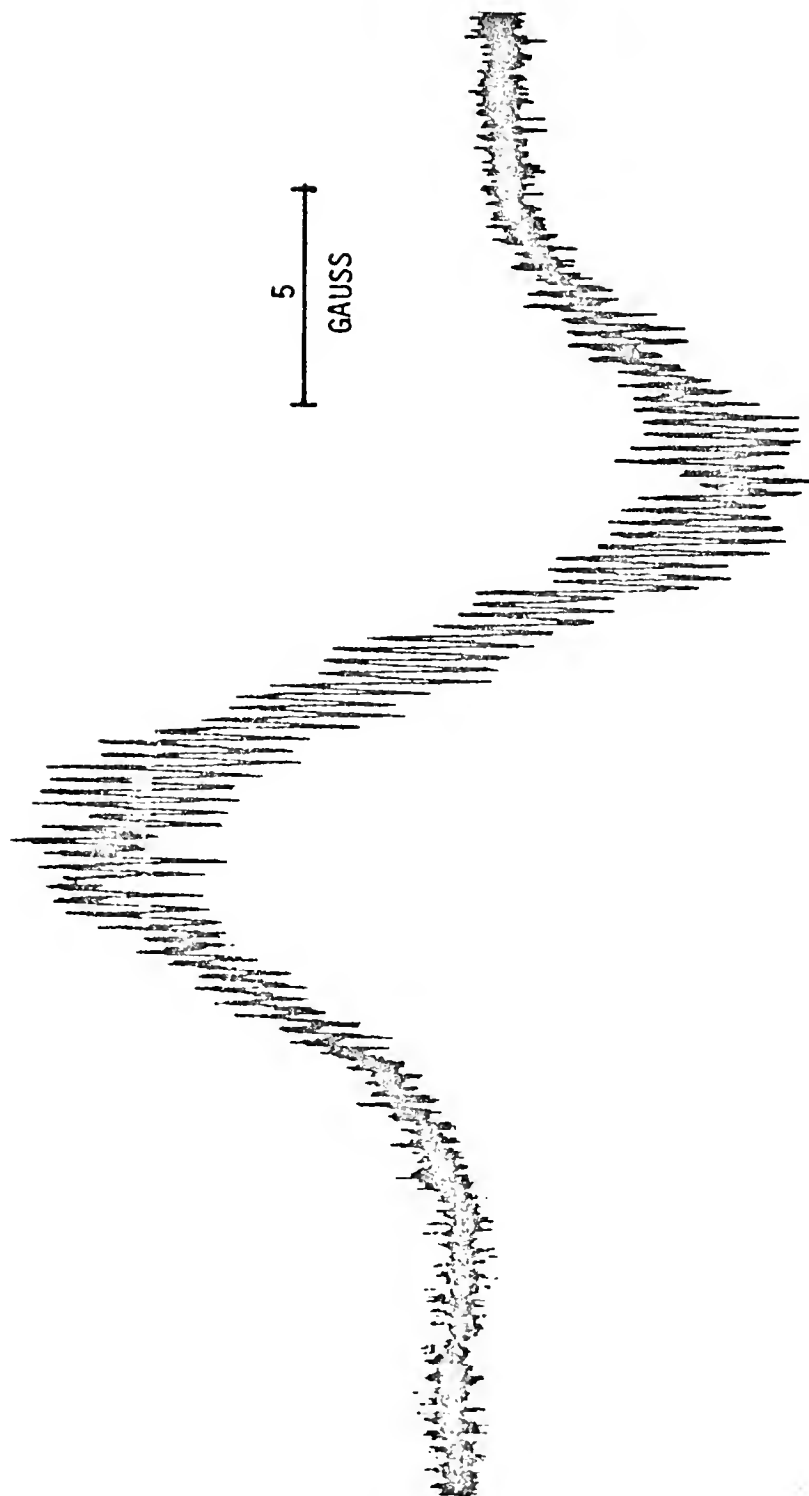


Figure 13. ESR Spectrum of Radical Derived From the Reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{PdCl}_2\text{L}_2$ ,  $\text{L} = (\text{C}_5\text{H}_4\text{N})(p\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{CCl}$ . Temp  $23^\circ$

The visible spectral data show that the absorption of longest wavelength is shifted to lower energy with the change from the cations to the corresponding radicals. This shift is 82 nm, 76 nm and 68 nm in going from  $\text{Ph}_3\text{C}^+$ ,  $(\text{p-CH}_3\text{C}_6\text{H}_4)_3\text{C}^+$  and  $(\text{p-ClC}_6\text{H}_4)_3\text{C}^+$  to the respective radicals. There is also a parallel shift to lower energy with the change from the complexed carbonium to the complexed radicals. The absorptions of lowest energy for the complexed  $(4\text{-C}_5\text{H}_4\text{N})\text{Ph}_2\text{C}^+$ ,  $(4\text{-C}_5\text{H}_4\text{N})(\text{p-CH}_3\text{C}_6\text{H}_4\text{N})_2\text{C}^+$  and  $(4\text{-C}_5\text{H}_4\text{N})(\text{p-MeOC}_6\text{H}_4)_2\text{C}^+$  are 457 nm, 492 nm and 537 nm, respectively,<sup>34</sup> whereas the values for the corresponding complexed radicals are 520 nm, 531 nm and 542 nm, respectively. The shifts are 63 nm, 39 nm and 5 nm, respectively. There is also a shift to lower energy from free base radical to coordinated base radical. The magnitude of the shifts are 19 and 21 nm, respectively, when the radicals are 4-pyridyldiphenylmethyl and 4-pyridyldi(p-tolyl)methyl. No explanation, at present, can be advanced for the magnitudes of such shifts. The absorptions of the uncomplexed cations containing a heterocyclic ring cannot be compared conveniently with those of the corresponding radicals because the values are reported for the protonated cations and the effect of this protonation on the position of the absorption peaks has yet to be evaluated. Thus, the only consistent trend observed is that the lowest energy visible absorption peaks of the free-radicals appear at longer wavelength than those of the corresponding cations.

The absorptions for the coordinated radicals also appear at longer wavelengths than those of the corresponding uncoordinated radicals. There is no simple explanation for these observations.

From the visible spectra it is deduced that the 4-pyridyldiaryl-methyl radicals are less stable with respect to their dimers than are

the triarylmethyl radicals. This is indicated by the rapid decay of intensity of the absorption spectra to almost zero absorbance in the case of 4-pyridyldiphenylmethyl and 4-pyridyldi(p-tolyl)methyl radicals presumably because of the following equilibrium which



lies farther to the right than for the non-heterocyclic triarylmethyl radicals. This result is expected on account of the electronegative N atom in the pyridyl ring which destabilizes the radical and hence favors the higher degree of dimerization.

#### Kinetics and Mechanism of the Reaction of Organic Halides With Tetrakis(triphenylphosphine)platinum(0)

The kinetics of the reaction were followed using  $1.23 \times 10^{-1} \text{M}$  triphenylmethyl chloride,  $1.91 \times 10^{-3} \text{M}$  tetrakis(triphenylphosphine)-platinum(0) and various concentrations of triphenylphosphine. The reaction followed second-order kinetics, first order in each reactant. Using a large excess (> 50-fold) of the halide, pseudo-first-order kinetics was obtained. The slope of the linear plots of  $\log (A-A_{\infty})$  vs time equals  $k_{\text{obsd}}/2.30$  and the rate constants so obtained were found to be different at different  $[\text{PPh}_3]$  (Table 2).

For the reaction of diphenylmethyl bromide with tetrakis(triphenylphosphine)platinum(0), it was found that a plot of  $k_{\text{obsd}}$  vs  $[\text{Ph}_2\text{CHBr}]/[\text{PPh}_3]$  was linear; but different slopes were obtained for each phosphine concentration. Two characteristic sets of data are presented in Figure 14. The data for these plots are tabulated in Table 3.

The observed kinetic behavior can be accommodated by the mechanism:



TABLE 2

Rate Constant Dependence on Initial Phosphine Concentration<sup>a</sup>

Initial $[\text{PPh}_3]$ , $\text{M} \times 10^3$	$10^2 \times k_{\text{obsd}}$ , $\text{sec}^{-1}$	$10 \times (k_{\text{obsd}}/[\text{Ph}_3\text{CCl}]) = k'$ , $\text{M}^{-1} \text{sec}^{-1}$
10.00	2.70	2.18
5.00	2.76	2.24
2.51	2.94	2.39
1.88	3.21	2.61
1.25	3.49	2.84
1.00	3.54	2.88
no $\text{P}(\text{C}_6\text{H}_5)_3$ added	3.72	3.02

<sup>a</sup> All rate constants are for:  $[\text{Ph}_3\text{CCl}] = 1.23 \times 10^{-1}\text{M}$  and  $[\text{Pt}(\text{PPh}_3)_4] = 1.91 \times 10^{-3}\text{M}$  and are measured at  $25^\circ$ .

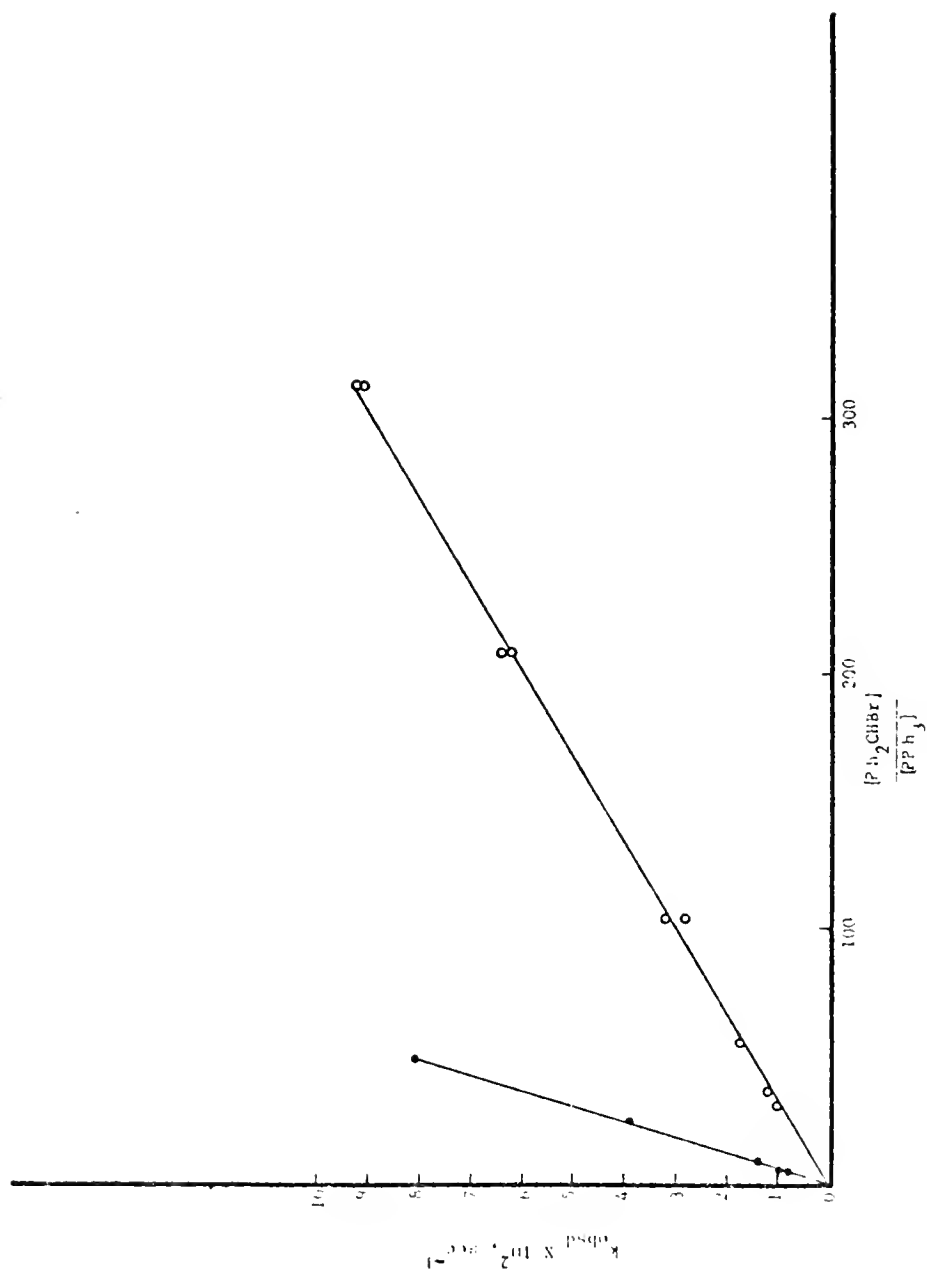


Figure 14. Plot of  $k_{\text{obsd}}$  vs  $\frac{[Ph_2CHBr]}{[PPh_3]}$  in Benzene at  $25^\circ$ . Dark circles are for  $4.7 \times 10^{-3} \text{ M PPh}_3$  and light circles are for  $8.0 \times 10^{-4} \text{ M PPh}_3$ .

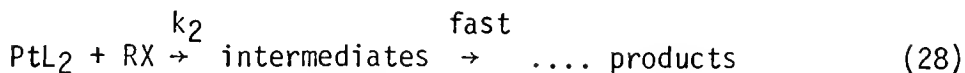
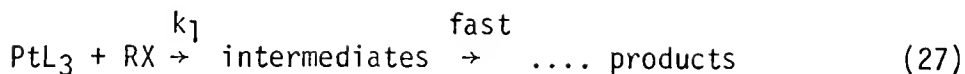
TABLE 3

$k_{\text{obsd}}$  as a Function of  $[\text{Ph}_2\text{CHBr}]/[\text{PPh}_3]$

$^a[\text{Ph}_2\text{CHBr}]/[\text{PPh}_3]$	$^a k_{\text{obsd}} \times 10^2$
312	9.2
208	6.3
104	3.1
55	1.8
36	1.2
31	1.0
49	8.1
25	3.9
9.5	1.4
6.3	0.95
5.4	0.83

<sup>a</sup> For first 6 entries,  $[\text{P}(\text{C}_6\text{H}_5)_3] = 8.0 \times 10^{-4}$

For last 5 entries,  $[\text{P}(\text{C}_6\text{H}_5)_3] = 4.7 \times 10^{-3}$



where  $\text{L} = \text{PPh}_3$  and  $\text{R} = \text{organic group}$ .

This gives rise to the rate law:

$$-\frac{d[\text{Pt(0)}]}{dt} = \frac{(k_1[\text{L}] + k_2K)[\text{RX}][\text{Pt(0)}]}{K + [\text{L}]} = k_{\text{obsd}}[\text{Pt(0)}] \quad (29)$$

Normalizing to a constant  $\text{RX}$  concentration,

$$k' = \frac{k_{\text{obsd}}}{[\text{RX}]} = \frac{k_1[\text{L}] + k_2K}{K + [\text{L}]} \quad (30)$$

As  $[\text{L}] \rightarrow \infty$ ,  $k' \rightarrow k_1$

As  $[\text{L}] \rightarrow 0$ ,  $k' \rightarrow k_2$

Rearranging equation (30) gives

$$k'(K + [\text{L}]) = k_1[\text{L}] + k_2K \quad (31)$$

From this, if  $K$  is known, the values  $k_1$  and  $k_2$  can be computed.

Using the  $k_{\text{obsd}}$  values of Table 2, one can plot  $k'(K + [\text{L}])$  vs  $[\text{L}]$  to obtain a straight line (Figure 15). From the intercept, the slope of this plot and the value of  $K = 1.6 \times 10^{-4} \text{M}$  obtained by Halpern and his co-workers<sup>45</sup>, values for  $k_1$  and  $k_2$  were calculated to be  $2.1 \times 10^{-1} \text{M}^{-1} \text{sec}^{-1}$  and  $7.3 \times 10^{-1} \text{M}^{-1} \text{sec}^{-1}$ , respectively.

In order to obtain some thermodynamic data from which one might be able to infer the nature of the transition states involved in the reactions between the  $\text{Pt(0)}$  complex with trityl chloride, benzhydryl bromide and with methyl iodide, the second-order rate constants,  $k'$ , were

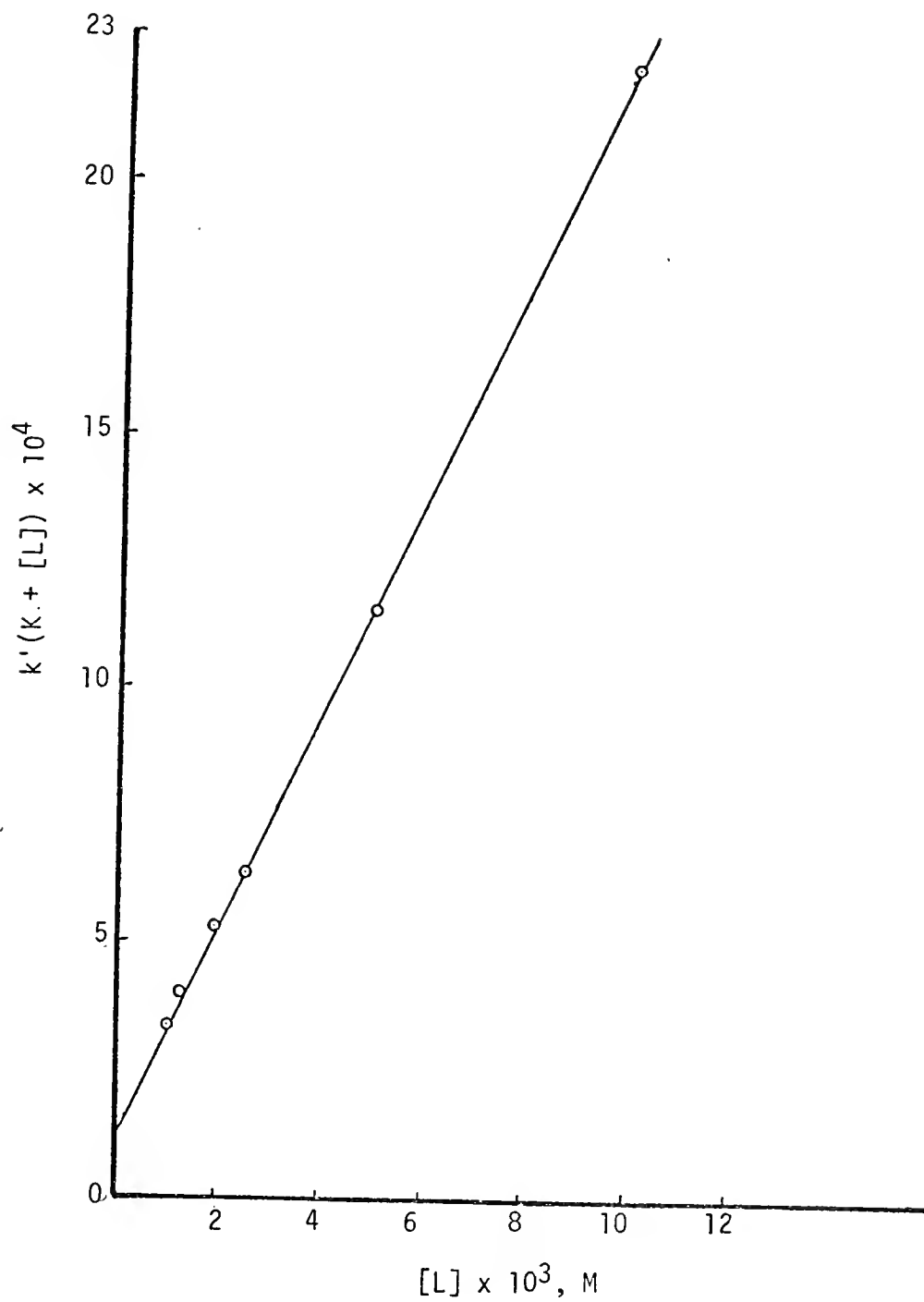


Figure 15. Plot of  $k'(K + [L])$  vs  $[L]$  in Benzene at  $25^\circ$

determined at several temperatures. The results of these determinations are tabulated in table 4. Since tris(triphenylphosphine)platinum(0) is in equilibrium with bis(triphenylphosphine)platinum(0) and free phosphine, an initial concentration of the excess triphenylphosphine was used to ensure that at least 98% of the platinum(0) complex was in the tricoordinated form. This calculation was based upon a constant of  $1.6 \times 10^{-4}M$  reported by Halpern and his coworkers.<sup>45</sup> This condition was satisfied by using an initial concentration of  $1.90 \times 10^{-3}M$   $Pt(PPh_3)_4$  and  $3.76 \times 10^{-2}M$   $PPh_3$  and was shown to be true from the estimated second-order rate constant which were experimentally the same at a given temperature when the excess triphenylphosphine concentration was either  $3.76 \times 10^{-2}M$  or  $1.16 \times 10^{-1}M$ . Similar concentrations of excess triphenylphosphine and tetrakis(triphenylphosphine)platinum(0) were used for the methyl iodide and diphenylmethyl bromide reactions.

In the case of methyl iodide, the kinetic runs were stopped when a precipitate of  $[PPh_3CH_3]I$  appeared (after about 30% reaction). However, the salt has very low solubility (concentrations  $> 5 \times 10^{-5}M$  bring about precipitation) and Pearson and Rajaram<sup>17</sup> have suggested that the reaction leading to the formation of this phosphonium salt may be a mildly competing reaction, but will have a negligible effect on the data since no spectral changes occur in the region of measurement.

Using the Arrhenius equation (32),

$$\log k' = \frac{\log A}{2.30} - \frac{\Delta E^\ddagger}{2.30 R} \cdot \frac{1}{T} \quad (32)$$

where  $k'$  = second-order rate constant

$A$  = pre-exponential factor

$\Delta E^\ddagger$  = activation energy

TABLE 4

Second-Order Rate Constants for the Reaction Between  $\text{Pt}(\text{PPh}_3)_4$   
and Organic Halides in Benzene

XY	Temp, °C	$k'$ , $\text{M}^{-1} \text{sec}^{-1}$ <sup>a</sup>
$(\text{C}_6\text{H}_5)_3\text{CCl}^{\text{b}}$	20.1	$1.49 \times 10^{-1}$ ( $1.51 \times 10^{-1}$ ) <sup>c</sup>
	22.4	$1.75 \times 10^{-1}$ ( $1.68 \times 10^{-1}$ )
	25.0	$1.91 \times 10^{-1}$ ( $1.91 \times 10^{-1}$ )
	27.6	$2.26 \times 10^{-1}$ ( $2.31 \times 10^{-1}$ )
	30.2	$2.55 \times 10^{-1}$ ( $2.58 \times 10^{-1}$ )
$\text{CH}_3\text{I}^{\text{d}}$	22.9	$3.28 \times 10^{-3}$
	25.0	$3.59 \times 10^{-3}$
	27.7	$4.16 \times 10^{-3}$
	30.8	$4.65 \times 10^{-3}$
$(\text{C}_6\text{H}_5)_2\text{CHBr}^{\text{e}}$	23.0	$2.63 \times 10^{-1}$
	25.0	$2.93 \times 10^{-1}$
	26.6	$3.17 \times 10^{-1}$
	28.6	$3.38 \times 10^{-1}$
	31.4	$3.89 \times 10^{-1}$

<sup>a</sup> Average from two kinetic runs.

<sup>b</sup> Initial concentrations:  $1.23 \times 10^{-1} \text{M}$   $\text{Ph}_3\text{CCl}$ ,  $1.91 \times 10^{-3} \text{M}$   $\text{PPh}_3$ .

<sup>c</sup> Values in parenthesis refer to the rate constants for  $1.16 \times 10^{-1} \text{M}$   $\text{PPh}_3$ . The average value for the 2 concentrations of  $\text{PPh}_3$  was used to determine the best fit plot.

<sup>d</sup> Initial concentrations:  $7.3 \times 10^{-1} \text{M}$   $\text{CH}_3\text{I}$ ,  $9.0 \times 10^{-4} \text{M}$   $\text{Pt}[\text{PPh}_3]_4$  and  $1.31 \times 10^{-2} \text{M}$   $\text{P}(\text{C}_6\text{H}_5)_3$ .

<sup>e</sup> Initial concentrations:  $7.1 \times 10^{-2} \text{M}$   $\text{Ph}_2\text{CHBr}$ ,  $1.07 \times 10^{-3} \text{M}$   $\text{Pt}(\text{PPh}_3)_4$  and  $1.37 \times 10^{-2} \text{M}$   $\text{PPh}_3$ .

R = ideal gas constant

T = absolute temperature

a plot of  $-\log k'$  vs  $1/T$  was found to be a straight line whose slope equals  $\Delta E^\ddagger/2.30 R$  and whose intercept equals  $\log A/2.30$  from which  $\Delta E^\ddagger$ , and A can be calculated. Using the relation

$$\Delta E^\ddagger = \Delta H^\ddagger + RT \quad (33)$$

and the Eyring equation

$$k' = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (34)$$

where k = Boltzmann's constant

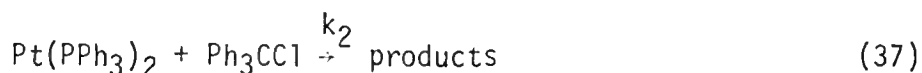
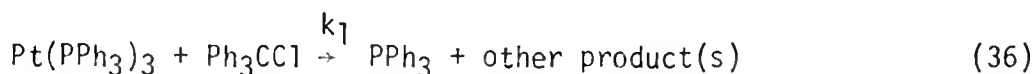
h = Planck's constant

$\Delta S^\ddagger$  can then be calculated.  $\Delta G^\ddagger$  was obtained from the relation

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (35)$$

The plots of the kinetic data are shown in figures 16-18 while the activation parameters estimated are listed in Table 5.

The kinetic behavior of the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  resemble that previously observed by Pearson and Rajaram for the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{CH}_3\text{I}$ <sup>17</sup>. These reactions follow overall second-order kinetics, first-order in  $\text{Pt}(\text{PPh}_3)_4$  and first-order in the halide. The  $k_{\text{obsd}}$  values are found to be dependent linearly on the value of  $[\text{RX}]/[\text{PPh}_3]$ , but the slopes of the linear plots are different for different phosphine concentrations (Table 3). Thus, the kinetic behavior of these reactions are consistent with the mechanism shown in equations (36) and (37)





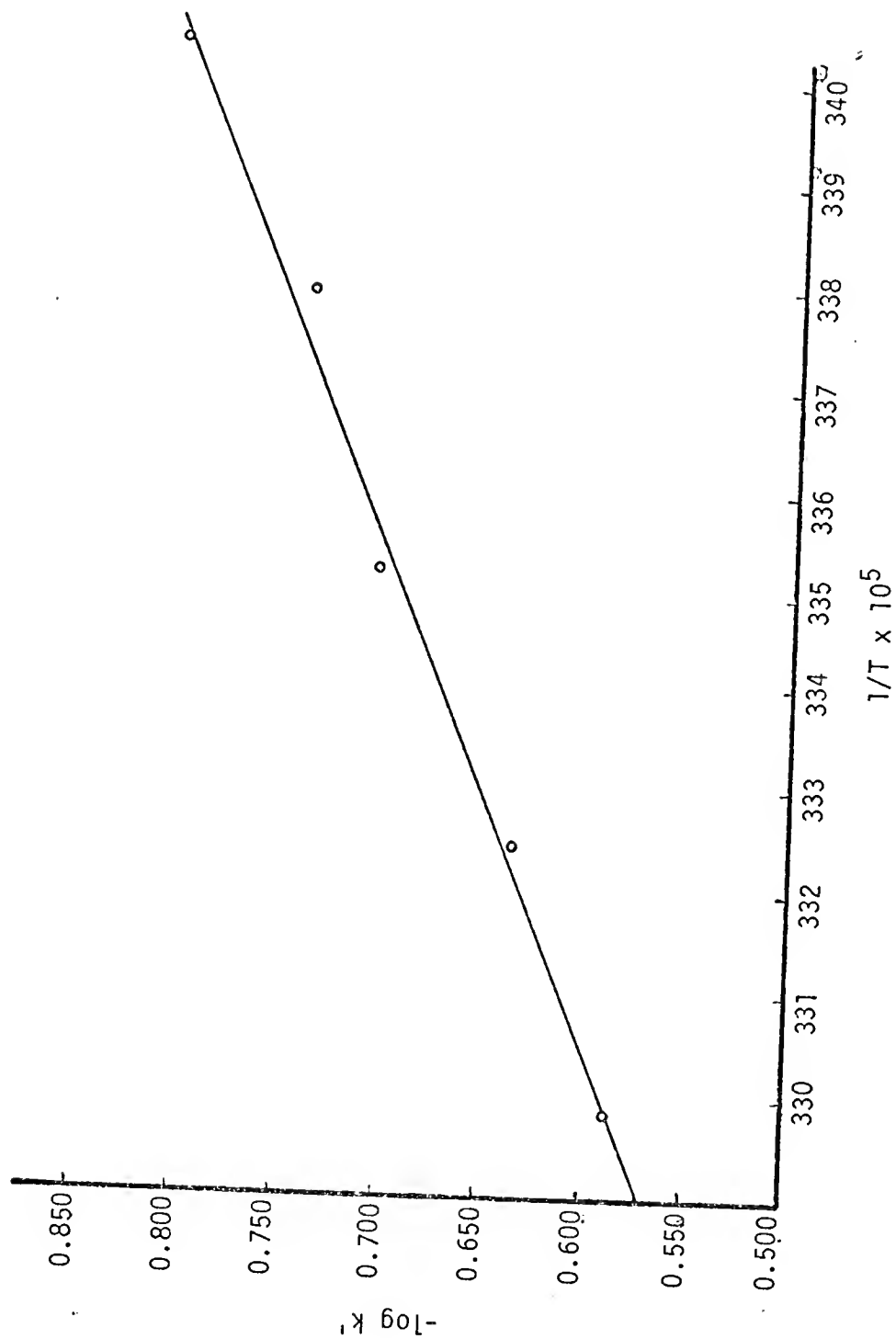


Figure 16. Plot of  $-\log k'$  vs  $1/T$  for the Reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{Ph}_3\text{CCl}$

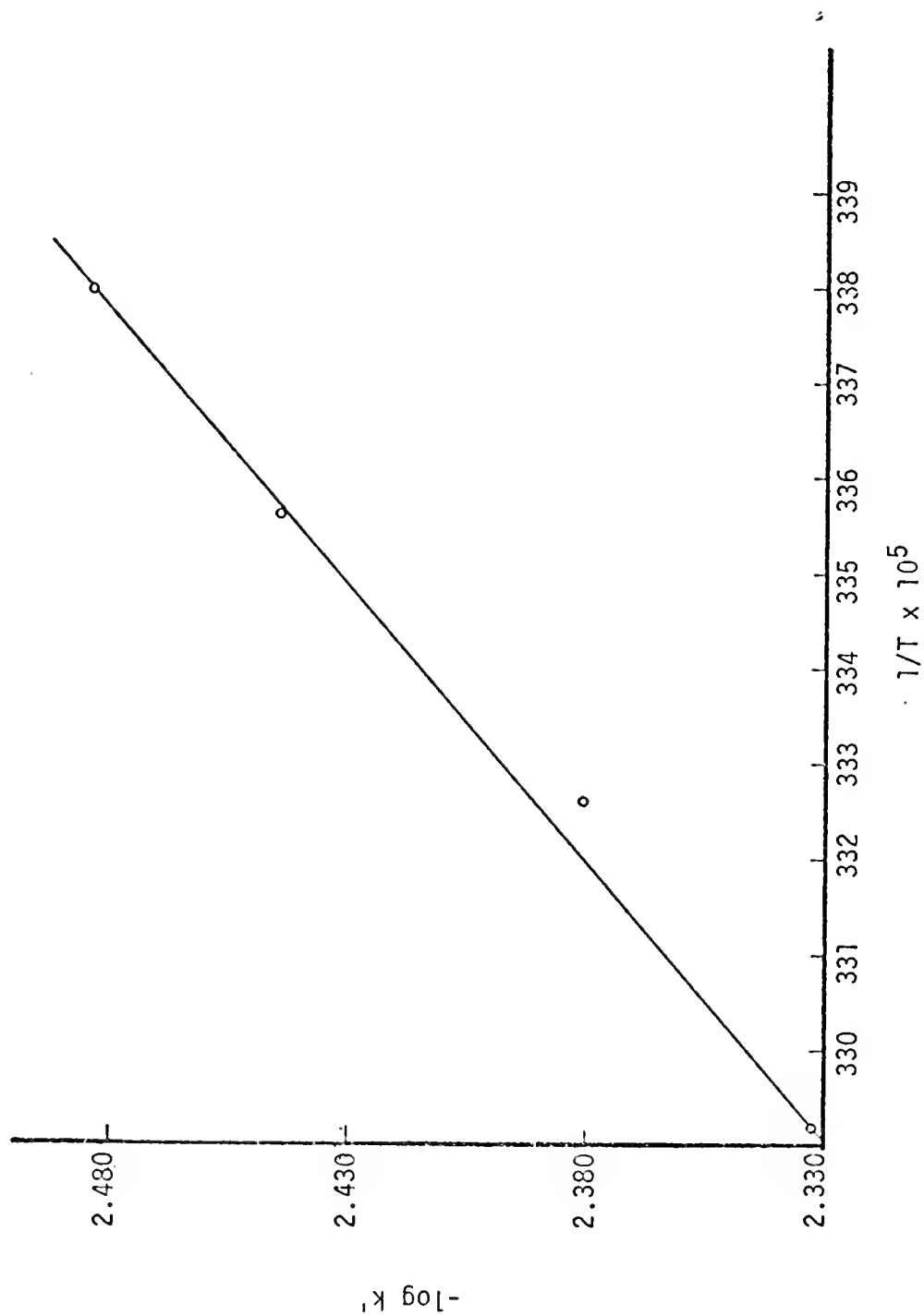


Figure 17. Plot of  $-\log k'$  vs  $1/T$  for the Reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{CH}_3\text{I}$

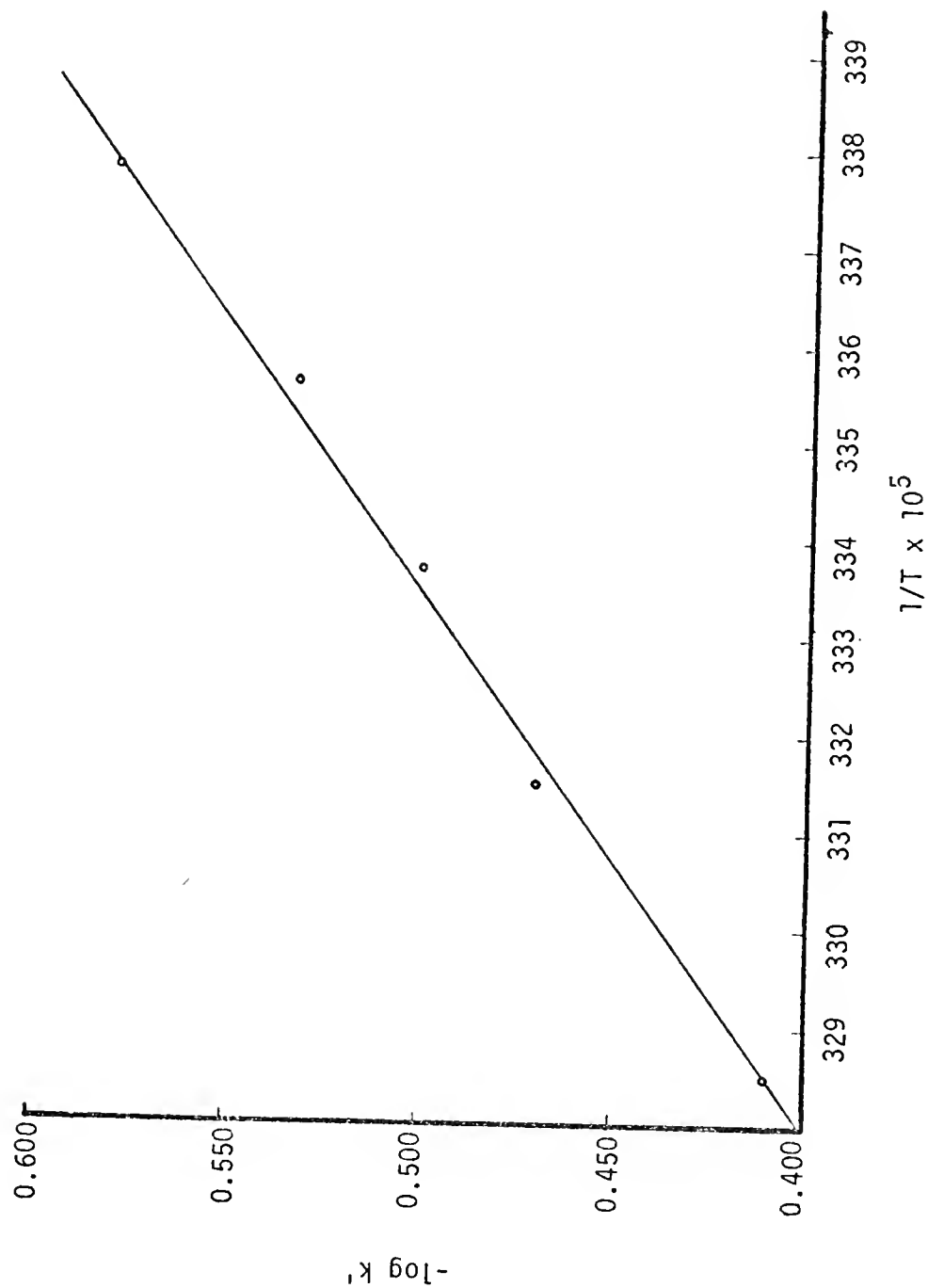


Figure 18. Plot of  $-\log k'$  vs  $1/T$  for the Reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{Ph}_2\text{CHBr}$

TABLE 5

Activation Parameters for the Reaction Between  $\text{Pt}(\text{PPh}_3)_4$  and Organic Halides at  $25^\circ$

XY	$k' \text{ (M}^{-1} \text{ sec}^{-1})$	$\Delta E^\ddagger \text{ (kcal/mole)}$	$\Delta S^\ddagger \text{ (eu)}$	$\Delta G^\ddagger \text{ (kcal/mole)}$	$D(R - X) \text{ (kcal/mole)}$
$\text{Ph}_3\text{CCl}$	$2.62 \times 10^{-1}$	9.4	-32	19	48
$\text{Ph}_2\text{CHBr}$	$2.93 \times 10^{-1}$	8.2	-32	18	44
$\text{CH}_3\text{I}$	$3.59 \times 10^{-3}$	5.1	-54	21	51

The rate constants  $k_1$  and  $k_2$  for the reactions were found to be  $2.1 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$  and  $7.3 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$  respectively. The corresponding values of Pearson and Rajaram for  $\text{CH}_3\text{I}$  are  $3.5 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$  and  $2.0 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ . Even though the faster rate of reaction of  $\text{Pt}(\text{PPh}_3)_3$  and  $\text{Pt}(\text{PPh}_3)_2$  with  $\text{Ph}_3\text{CCl}$  as compared to the reaction of the  $\text{Pt}(0)$  complex with  $\text{CH}_3\text{I}$  is consistent with the lower carbon-halogen bond dissociation energy of  $\text{Ph}_3\text{CCl}$  compared to that of  $\text{CH}_3\text{I}$ , no correlation between rate and bond dissociation energy can be made. The reason is because the mechanisms for the reaction of these halides with  $\text{Pt}(\text{PPh}_3)_4$  are different, as will be demonstrated later.

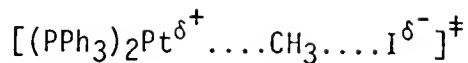
Although the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{CH}_3\text{I}$ ,  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  exhibit similar kinetic behavior, the products are not analogous. Whereas the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{CH}_3\text{I}$  yields the normal oxidative-addition product  $\text{PtICH}_3(\text{PPh}_3)_2$ , the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  yields  $\text{Ph}_3\text{C}\cdot$  (and the dimer) and  $\text{Ph}_2\text{CH}-\text{CHPh}_2$ , respectively. The other products are cis- $\text{PtCl}_2(\text{PPh}_3)_2$  and cis- $\text{PtBr}_2(\text{PPh}_3)_2$ , respectively. Thus, the details of the mechanism of these reactions must be different. The reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{CH}_3\text{I}$  has been proposed to proceed via a polar transition state on the basis of an increase in rate with an increase in polarity of the solvent used<sup>17</sup>; and as stated earlier, one objective of this work is to determine if the mechanism of analogous reactions with tertiary and secondary halides such as  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  proceed via free-radical intermediates.

In the estimation of the activation parameters of the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with the three halides, the concentration of  $\text{PPh}_3$  was chosen such that the tricoordinated  $\text{Pt}(0)$  complex,  $\text{Pt}(\text{PPh}_3)_3$ , was equal to the total initial  $\text{Pt}(0)$  concentration. Under this condition the activation

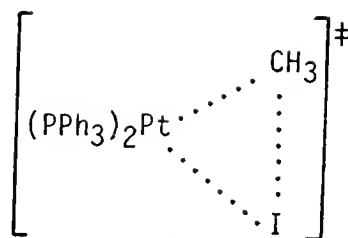
parameters obtained are for the principal reaction between  $\text{Pt}(\text{PPh}_3)_3$  and  $\text{RX}$ , where  $\text{RX} = \text{Ph}_3\text{CCl}$ ,  $\text{Ph}_2\text{CHBr}$  and  $\text{CH}_3\text{I}$ . The values of  $k'$  at  $25^\circ$  ( $\text{M}^{-1} \text{sec}^{-1}$ ), of  $\Delta E^\ddagger$  (kcal/mole), of  $\Delta S^\ddagger$  (eu) and of  $\Delta G^\ddagger$  (kcal/mole), respectively, were determined to be:  $\text{Ph}_3\text{CCl}$ ,  $2.6 \times 10^{-2}$ , 9.4, -32 and 19;  $\text{Ph}_2\text{CHBr}$ ,  $2.93 \times 10^{-1}$ , 8.2, -32 and 18; and  $\text{CH}_3\text{I}$ ,  $2.59 \times 10^{-3}$ , 5.1, -54 and 21. The  $\Delta E^\ddagger$  values of between 5.1 to 9.4 kcal/mole are in the same range as those cited for the reaction of other organic halides with  $\text{Co}(\text{CN})_5^{3-}$ ; but, no correlation between the enthalpy of activation can be deduced from the data. However, the free energy of activation,  $\Delta G^\ddagger$ , in the order  $\text{Ph}_2\text{CHBr} < \text{Ph}_3\text{CCl}$  is consistent with the reverse order  $\text{Ph}_3\text{CCl} < \text{Ph}_2\text{CHBr}$  for the rate constants. Furthermore, the order for the  $\Delta G^\ddagger$  values parallels the order for the bond dissociation energies of  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$ . Thus, the reactivity of  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  with  $\text{Pt}(\text{PPh}_3)_3$  depends, at least in part, on the carbon-halogen bond strength of the halides. It should be noted that these correlations cannot be extended to  $\text{CH}_3\text{I}$  since a different mechanism is involved.

The entropies of activation (-32 eu for  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  and -54 eu for  $\text{CH}_3\text{I}$ ) are unexpectedly negative for reactions involving uncharged reactants and products. It is of interest to note that  $\Delta S^\ddagger$  for  $\text{CH}_3\text{I}$ , in which  $\text{PtICH}_3(\text{PPh}_3)_2$  is the oxidative product, is some 22 eu more negative than that for  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  in which the dihalobis(triphenylphosphine)platinum(0) is the  $\text{Pt}(\text{II})$  product. A large negative entropy of activation has been attributed to either a marked increase in polarity, or unusually stringent stereochemical requirements, in going from reactants to the transition state<sup>18,46</sup>. For  $\text{CH}_3\text{I}$ , the increase in rate with increase in polarity of the solvent has been adduced to a polar transition state of type (I) rather than

type (II).<sup>17</sup>



(I)



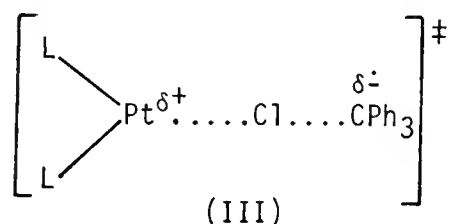
(II)

The reaction of trans-IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> with CH<sub>3</sub>I has been shown to involve an analogous polar transition state, the estimated  $\Delta E^{\ddagger}$  and  $\Delta S^{\ddagger}$  values of 6.2 kcal/mole and -51 eu, respectively, being remarkably close to the corresponding values for the Pt(0) reaction with CH<sub>3</sub>I. Analogous transition states cannot be ascribed to reaction of the Pt(0) with Ph<sub>3</sub>CCl and Ph<sub>2</sub>CHBr for steric reasons. Indeed, solvolytic displacement reactions of Ph<sub>3</sub>CCl and Ph<sub>2</sub>CHBr proceed via an S<sub>N</sub>1 rather than an S<sub>N</sub>2 mechanism.

As mentioned earlier, there is a relatively large difference of some 22 eu in  $\Delta S^{\ddagger}$  when the halide is changed from CH<sub>3</sub>I to Ph<sub>3</sub>CCl or Ph<sub>2</sub>CHBr. There is also an increase in rate of reaction with increase in polarity of the solvent. (The magnitude of this increase has not been determined because the rate is too fast to be measured by conventional methods.) If it is first assumed that a polar transition state, analogous to the one in the case of CH<sub>3</sub>I is formed, the less negative  $\Delta S^{\ddagger}$  (compared to CH<sub>3</sub>I) cannot be rationalized on the basis of a more constrained transition state since one would expect then that  $\Delta S^{\ddagger}$  for the larger Ph<sub>3</sub>CCl and Ph<sub>2</sub>CHBr would be more negative than that obtained for CH<sub>3</sub>I. However, one can argue that, since the reactions are carried out in benzene, and Ph<sub>3</sub>CCl and Ph<sub>2</sub>CHBr are aromatic, the solvent molecules around the halide molecules are somewhat ordered but are "squeezed" out in the transition state resulting in a less negative  $\Delta S^{\ddagger}$ . One would also have to submit that this solvent effect predominates over the steric factor in the transition state so that

the net result is a less negative  $\Delta S^\ddagger$  for  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$ . If this were the situation, then it also follows that  $\Delta S^\ddagger$  for  $\text{Ph}_2\text{CHBr}$  should be more negative than  $\text{Ph}_3\text{CCl}$  since the solvent effect should be less with  $\text{Ph}_2\text{CHBr}$  which has only 2 aromatic rings compared to 3 in  $\text{Ph}_3\text{CCl}$ , but  $\Delta S^\ddagger$  is the same for both. Hence, transition state of type (I) may not be operative in the reaction of  $\text{Pt}(0)$  with  $\text{Ph}_3\text{CCl}$  or  $\text{Ph}_2\text{CHBr}$  on the basis of activation parameter data also. The second possible transition state (type (II)) is relatively non-polar and contradicts the experimental fact that the rate of reaction is enhanced by using a more polar solvent. Moreover, such a transition state would dictate a more stringent stereochemical requirement in the transition state for the larger  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  molecules leading to a more but negative  $\Delta S^\ddagger$  for  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$ , but instead the reverse has been found.

A third type of transition state (type (III)) can be considered for oxidative addition of the  $\text{Pt}(0)$  complex to  $\text{Ph}_3\text{CCl}$  or  $\text{Ph}_2\text{CHBr}$ . This consideration arises out of the different products of the reaction which may be the result that a new mechanism is operative. Such a

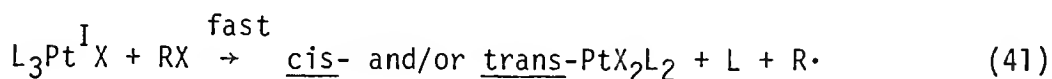
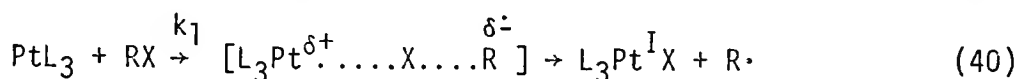


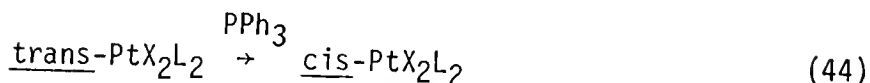
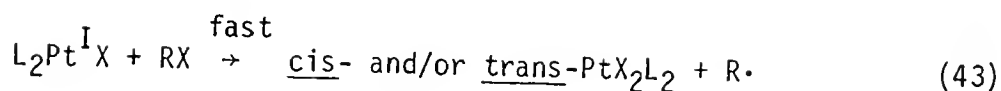
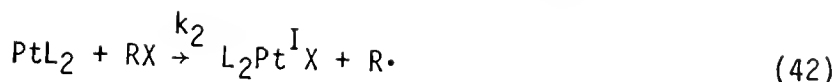
transition state, which is assumed to have more product-like ( $\text{Ph}_3\text{C}\cdot$  and  $\text{L}_2\text{PtCl}$ ) than reactant-like character, would be attractive for three reasons. Firstly, it would explain that, for example,  $\text{Ph}_3\text{C}\cdot$  is formed in the reaction of  $\text{Pt}(0)$  with  $\text{Ph}_3\text{CCl}$  but  $\text{CH}_3\cdot$  is not formed with  $\text{CH}_3\text{I}$ . The reason is that such a transition state, leading to the relatively unstable  $\text{CH}_3\cdot$  is energetically prohibitive, whereas transition



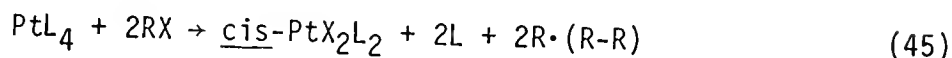
state of type (I), leading to the formation of the normal oxidative-addition product is now preferred. On the other hand, type (II) transition state would be unfavorable for  $\text{Ph}_3\text{CCl}$  because of steric reasons. With  $\text{Ph}_2\text{CHBr}$ , the relatively stable (cf  $\text{CH}_3\cdot$ ) diphenylmethyl radicals, once generated, are unstable with respect to the dimer and hence  $\text{Ph}_2\text{CH-CHPh}_2$  is obtained as the organic product. Secondly, the proposed transition state is not at variance with the activation parameters obtained. There is little difference in  $\Delta S^\ddagger$  for both  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$  because the solvent molecules are not displaced from the vicinity of the aromatic rings since they are farther from the reaction site than they would be if type (I) transition state were operative. Furthermore, the more negative  $\Delta S^\ddagger$  for  $\text{CH}_3\text{I}$  can be rationalized on the basis of less carbon-halogen bond breaking in the transition state so that the decrease of entropy is greater. Finally, the proposed transition state is a polar one and is consistent with the increase in rate with increase in polarity of the solvent.

From the above discussion on the kinetics and transition state of the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$ , a mechanism for the reaction consistent with the kinetics and activation parameters, can now be proposed as follows:





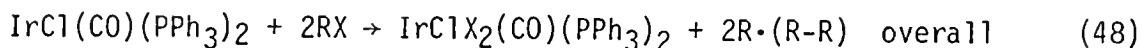
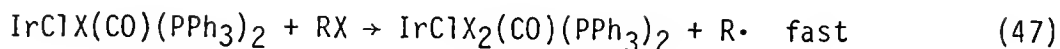
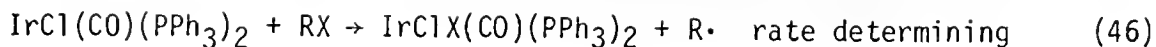
The overall reaction is thus:



In spite of the activation parameter data, one might argue that the reaction proceeds via a normal oxidative addition to form  $\text{PtCl}(\text{Ph}_3\text{C})-(\text{PPh}_3)_2$ , followed by a second oxidative addition forming  $\text{PtCl}_2(\text{Ph}_3\text{C})_2-(\text{PPh}_3)_2$  which then undergoes reductive elimination to give cis- $\text{PtCl}_2(\text{PPh}_3)_2$  and  $\text{Ph}_3\text{C-CPh}_3$ , the latter dissociating to give  $\text{Ph}_3\text{C}\cdot$ . If this were so, then, one should be able to isolate the first oxidative-addition product  $\text{PtCl}(\text{Ph}_3\text{C})(\text{PPh}_3)_2$  especially with less than the stoichiometric amount of  $\text{Ph}_3\text{CCl}$ . Attempts to isolate either  $\text{PtCl}(\text{Ph}_3\text{C})(\text{PPh}_3)_2$  or  $\text{PtCl}(\text{Ph}_3\text{CH})-(\text{PPh}_3)_2$  were unsuccessful. Even though the relatively unstable  $\text{PtCl}(\text{Ph}_3\text{C})(\text{PPh}_3)_2$  were formed, it seems unreasonable to expect a further molecule of the bulky  $\text{Ph}_3\text{CCl}$  to add more rapidly than the first. Thus, the proposed free-radical mechanism appears to be quite sound.

In order to extend the free-radical reactions of tertiary and secondary aromatic halides to  $d^8$  systems and perhaps also to find more corroborating evidence for the radical nature of the mechanistic pathway, the reactions of trans-chlorocarbonylbis(triphenylphosphine)-iridium(I) with  $\text{Ph}_3\text{CBr}$  and  $\text{Ph}_2\text{CHBr}$  were carried out. When  $\text{Ph}_3\text{CBr}$  was added to a benzene solution of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , the yellow solution

immediately turned orange and an esr spectrum of the solution showed the presence of  $\text{Ph}_3\text{C}\cdot$ . On stirring for 3 hours, > 80% yield of  $\text{IrBr}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$  was obtained. In a similar manner, using  $\text{Ph}_2\text{CHBr}$  instead of  $\text{Ph}_3\text{CBr}$ , yields  $\text{IrBr}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Ph}_2\text{CH-CHPh}_2$  in nearly quantitative yield after 12 hours' reaction. These two reactions strongly reinforce the assertion of a free-radical mechanism since  $\text{Ph}_3\text{C}\cdot$  and  $\text{Ph}_2\text{CHCHPh}_2$  could not have arisen from two successive oxidative additions of the halide to  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ . The first oxidative-addition step would have formed the  $\text{IrBrCl}(\text{Ph}_3\text{C})(\text{CO})(\text{PPh}_3)_2$  which is coordinately saturated and a second oxidative addition of  $\text{Ph}_3\text{CBr}$  would have yielded an extremely improbable octa-coordinated  $\text{Ir}^{\text{V}}$  species. It should also be mentioned that the oxidative addition of methyl halides,  $\text{CH}_3\text{X}$ , to trans- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  to form  $\text{IrXCl}(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$  is well documented<sup>18,47</sup> and no further reaction of  $\text{CH}_3\text{I}$  with  $\text{IrClI}(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$  has ever been found. Finally, when  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  was reacted with a mixture of  $\text{Ph}_3\text{CBr}$  and  $\text{Ph}_2\text{CHBr}$  in an equimolar ratio of all three reactants, the products of the reaction were found to be  $\text{IrBr}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and pentaphenylethane. The pentaphenylethane was identified by its mass spectrum which showed intense peaks corresponding to  $m/e$  243 and 167 which were assigned to the  $\text{Ph}_3\text{C}^+$  and  $\text{Ph}_2\text{CH}^+$  ions. Two peaks of considerably weaker intensity at  $m/e$  410 and 333 corresponding to the parent molecular ion and  $\text{Ph}_4\text{C}_2\text{H}^+$  were also observed. This experiment provides further evidence for a free-radical reaction of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with  $\text{Ph}_3\text{CBr}$  and  $\text{Ph}_2\text{CHBr}$ . The pentaphenylethane is presumably formed by combination of  $\text{Ph}_3\text{C}\cdot$  and  $\text{Ph}_2\text{CH}\cdot$  radicals. Thus, a new free-radical mechanism for the reaction of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with tertiary and secondary aromatic halides can be proposed as follows:



where R = tertiary or secondary aromatic group

X = halogen

It is not possible at this time to determine the precise nature of the transition state. This information must await the results of experiments for the determination of activation parameters and rate dependence on the polarity of solvents. It would also be of interest to study the effect of rate of reaction when one varies the halogen on both the halide and the Ir(I) complex.

#### Reactions of Tetrakis(triphenylphosphine)platinum(0) With Interhalogens

The preceding discussion has focused on the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with organic halides which have been demonstrated to react in two ways. A primary halide such as  $\text{CH}_3\text{I}$ , adds oxidatively to form trans- $\text{PtICH}_3(\text{PPh}_3)_2$ ,<sup>17</sup> whereas, secondary and tertiary aromatic halides yield cis-dihalogenobis(triphenylphosphine)platinum(II). In the midst of the work just described, the interest to investigate the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with interhalogens was aroused. Questions such as these were asked: (1) Will the interhalogens add oxidatively to the Pt(0) complex analogously to  $\text{CH}_3\text{I}$  to form new, mixed dihalogenobis-(triphenylphosphine)platinum(II)? Or (2) Will they react to form dihalogenobis(triphenylphosphine)platinum(II) complexes containing only one type of halogen in a reaction analogous to that with triarylmethyl halides? (3) What is the stereochemistry of the products and how do these products come about? Thus, in an

attempt to answer some of these questions, the investigation of the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with interhalogens was initiated.

The choice of the interhalogens, namely, iodine monobromide and iodine monochloride, was dictated by their stability with respect to disproportionation and by their commercial availability. When  $\text{Pt}(\text{PPh}_3)_4$  was reacted with  $\text{ICl}$  in 1:6, 1:3 and 1:1.2 mole ratios, the pre-dominant, halogen-containing Pt(II) species were found to be trans- $\text{PtCl}_2(\text{PPh}_3)_2$  (74%), trans- $\text{PtI}_2(\text{PPh}_3)_2$  (> 80%) and cis- $\text{PtClI}(\text{PPh}_3)_2$ , respectively. The trans- $\text{PtI}_2(\text{PPh}_3)_2$  and trans- $\text{PtCl}_2(\text{PPh}_3)_2$  were identified by decomposition point, elemental analysis and by comparison of their ir spectra with those published. It is worthwhile to point out at this time that Mastin<sup>36</sup> has proposed that in complexes of the type  $\text{PtX}_2(\text{PPh}_3)_2$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ , the cis- or the trans-isomer can be differentiated by examination of the ir spectra in the region  $480\text{-}550\text{ cm}^{-1}$ . In cis-isomers, the ir spectra contain a strong absorption at  $550 \pm 5\text{ cm}^{-1}$  whereas, this same absorption is relatively weak in the trans-isomer. This difference is clearly illustrated in cis- and trans-dibromobis(triphenylphosphine)platinum(II) (figures 19 A and B). This observation was utilized time and again to differentiate the cis- from the trans-isomers. Furthermore, several additional generalizations may be made concerning the differences between the cis- and the trans-isomers: (1) Cis-isomers are usually less colored than trans-isomers. (2) The solubility in non-polar solvents is greater for the trans-isomers. (3) The decomposition point is higher for the trans-isomer than for the cis-isomer. (4) For the two weak absorptions just below  $1600\text{ cm}^{-1}$  and which are present in the ir spectra of both isomers, the more intense one appears at higher energy

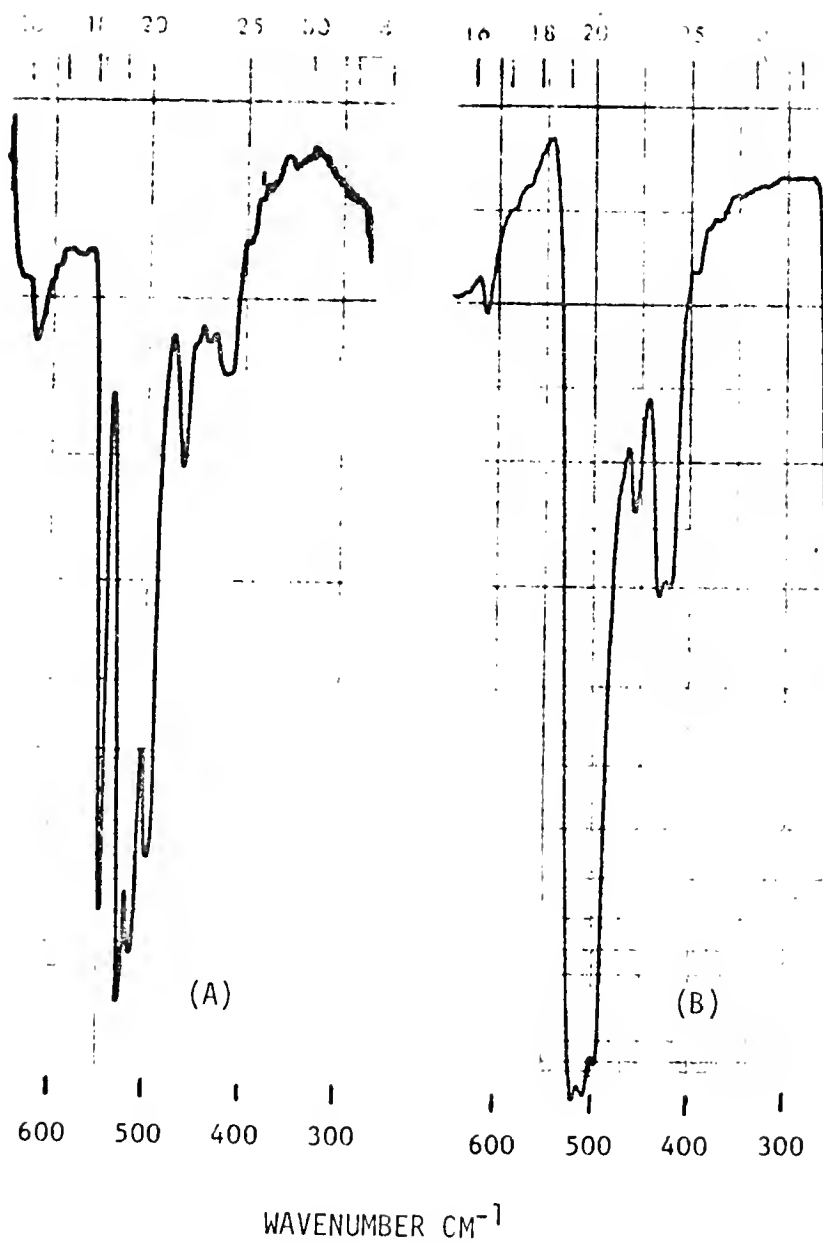


Figure 12. Infrared Spectrum of (A) Cis- and (B) Trans- $\text{PtBr}_2(\text{PPh}_3)_2$

in the spectra of the trans-isomer. This last generalization was first reported by Bland and Kemmitt<sup>48</sup>.

The reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{ICl}$  in a 1:6 mole ratio provides the quickest synthetic route and the highest yield (74%) so far reported for the preparation of trans-dichlorobis(triphenylphosphine)platinum(II). Conventional methods of synthesis yield only the cis-isomer. The most recently published preparation of the trans-isomer involves photochemical isomerization of the cis-isomer with a reported yield of 40%<sup>49</sup>. Besides the relatively low yield, the photochemical preparation takes a much longer reaction time (4 hours). It also suffers from the undesirable necessity of having to separate one desired isomer from a mixture containing both isomers. This results in lower yields in the purification process if pure isomer is required. The present method, using  $\text{Pt}(\text{PPh}_3)_4$  and  $\text{ICl}$ , requires only a few minutes of reaction time and results in the formation of the trans-isomer in high yield.

With a mole ratio of  $\text{Pt}(\text{PPh}_3)_4$  to  $\text{ICl}$  of 1:3 the product is trans- $\text{PtI}_2(\text{PPh}_3)_2$ . This result is rather surprising in view of the product got from the 1:6 addition, viz., trans- $\text{PtCl}_2(\text{PPh}_3)_2$ . Firstly, one would expect the  $\text{ICl}$  to serve in its usual capacity as a chlorinating agent. Secondly, this oxidative addition is quite different from the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{CH}_3\text{I}$  and  $\text{Ph}_3\text{CCl}$  discussed previously. The "normal" oxidative product is not isolated as in the reaction with  $\text{CH}_3\text{I}$  and the reaction is different from that of  $\text{Ph}_3\text{CCl}$  in that the halogen atoms coordinated to the Pt atom is the more electropositive end of the molecule  $\text{ICl}$ , whereas, for  $\text{Ph}_3\text{CCl}$ , the Cl atom is the more electronegative portion of the molecule.

In an attempt to isolate any stable precursors of trans-PtI<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub>, the reaction of Pt(PPh<sub>3</sub>)<sub>4</sub> with ICl was again carried out using a 1:1 mole ratio of the reactants. In this reaction, only about 60% of the Pt metal was precipitated as halogeno-Pt(II) after the usual work-up; the reason for this can be attributed to competition for ICl by the platinum(0) and free PPh<sub>3</sub>, the latter of which rapidly forms PPh<sub>3</sub>ICl<sup>50</sup>. The precipitated product was found to contain predominantly cis-PtClI(PPh<sub>3</sub>)<sub>2</sub> and some trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. This cis-isomer of PtClI(PPh<sub>3</sub>)<sub>2</sub> was inferred from the ir spectrum which contained the strong absorption at 550 cm<sup>-1</sup> characteristic of the cis-isomer.

In the foregoing discussion, the discovery that the reaction of Pt(PPh<sub>3</sub>)<sub>4</sub> with ICl gives rise to three distinct Pt(II) complexes depending upon the relative amounts of the reactants employed, was presented. But, how can these diverse products be rationalized? Let us first consider the formation of trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. If it is assumed that ICl adds oxidatively to Pt(PPh<sub>3</sub>)<sub>4</sub> to form first trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>, there remains the problem of accounting for the subsequent transformation of trans-PtClI(PPh<sub>3</sub>)<sub>2</sub> to trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. Two plausible routes will be considered: (1) A second molecule of ICl can undergo a second oxidative addition to trans-PtClI(PPh<sub>3</sub>)<sub>2</sub> to form an octahedral Pt(IV) complex which subsequently undergoes a reductive elimination of Cl<sub>2</sub>, or (2) a substitution reaction can occur in which a chloride ion is replaced by an iodide ion upon attack of ICl. The possibility of a second oxidative addition of ICl to trans-PtClI(PPh<sub>3</sub>)<sub>2</sub> yielding an octahedral complex, which subsequently undergoes a reductive elimination, can be ruled out in this system since, if the octahedral complex were formed, it would be expected to be quite stable under the reaction conditions and time employed

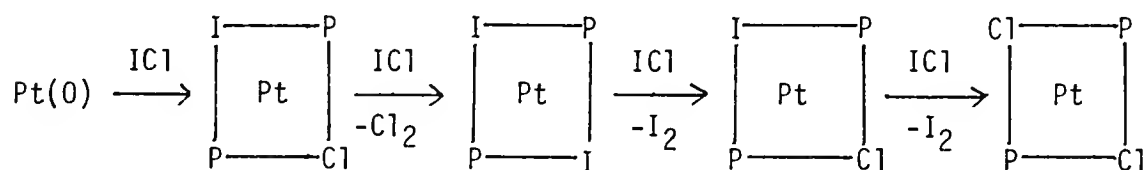


(5 minutes). Furthermore, there is evidence that when a dihalogenobis(triphenylphosphine)platinum(II) reacts with an interhalogen, substitution reactions occur faster than addition reactions. In many of these types of reactions to be discussed later, the substitution products are isolated, but, if the reaction time is increased, Pt(IV) complexes are formed. This observation suggests that in a system containing dihalogenobis(triphenylphosphine)platinum(II) and an interhalogen, the thermodynamically stable species is tetrahalogenobis(triphenylphosphine)platinum(IV). This observation lends support to the earlier argument against reductive elimination. Thus, based upon the assigned premise trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is produced as a consequence of a substitution reaction of ICl on trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>.

A rather obvious question arises, however. Why should trans-PtClI(PPh<sub>3</sub>)<sub>2</sub> be proposed as a precursor to trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> when cis-PtClI(PPh<sub>3</sub>)<sub>2</sub> is the isolated product in the 1:1 addition? The compelling reason is that substitution reactions involving square planar Pt(II) complexes are stereospecific, i.e., substitution reactions involving cis- and trans-complexes yield cis- and trans-isomers, respectively<sup>51-54</sup>. No exceptions have been reported. Furthermore, stereospecificity obtains in all the substitution reactions of Pt(II) complexes studied during the course of this work. If trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> must be formed from trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>, one must account for the observation that the only mixed halogeno-complex isolated was cis-PtClI(PPh<sub>3</sub>)<sub>2</sub>. These seemingly contradictory "truths" can be accounted for by assuming that, after the initial formation in solution of trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>, the excess of free phosphine causes rapid isomerization to the cis-PtClI(PPh<sub>3</sub>)<sub>2</sub> which precipitates from

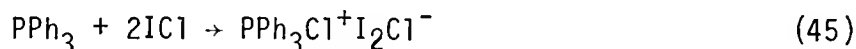
the reaction mixture, the low solubility of the cis-isomer in benzene contributing significantly to the driving force of the reaction. It is well known that free phosphine catalyses isomerization of this kind. Allen and Baird reported that on addition of a trace of tri-phenylphosphine to a chloroform solution of trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, the yellow color of the solution is rapidly discharged resulting in the cis-isomer<sup>55</sup>. This rapid isomerization was also demonstrated in this laboratory to occur in benzene solution whereupon cis-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> precipitated out.

The product obtained when Pt(PPh<sub>3</sub>)<sub>4</sub> reacts with ICl in a 1:6 mole ratio is trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. Initially, one might be tempted to assume that the trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>, which is formed first, would be converted into trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> which, subsequently, undergoes halogen substitution to form trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. This assumption would seem to be substantiated by the observed conversion by ICl of trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> to trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. However, upon examination of the reaction sequence shown below, it can be seen that



there is a flaw, albeit a subtle one; namely, the formation of both trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> from the same species, trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>. The final product, trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, which is more thermodynamically stable than trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the presence of ICl, must be formed directly from trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>. If this be so, the question arises as to why trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is the predominant

product when the ratio of Pt(0) to ICl is 1:3. Accordingly, it is proposed that when the 1:3 ratio obtains, trans-PtClI(PPh<sub>3</sub>)<sub>2</sub> is, as usual, formed first. But the subsequent attacking species is not ICl, but another species. If it were ICl, trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> would result as discussed above. The most probable attacking species is I<sub>2</sub>Cl<sup>-</sup> which will be formed from the reaction of PPh<sub>3</sub> and ICl according to equation (45)



This rapid reaction is analogous to the reaction of PPh<sub>3</sub> with IBr to form PPh<sub>3</sub>Br<sup>+</sup>I<sub>2</sub>Br<sup>-</sup><sup>50</sup>. Analogous ionic species, in which the halogen bound to the Group VA element is the one of lower atomic number, are also formed with the reaction of triphenylarsine with IBr<sup>50,56</sup>. Thus, when the mole ratio of Pt(PPh<sub>3</sub>)<sub>4</sub> to ICl is 1:3, there is very little ICl to react with the trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>. Instead, the resulting attack by I<sub>2</sub>Cl<sup>-</sup> on trans-PtClI(PPh<sub>3</sub>)<sub>2</sub> yields trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. All the products in the reaction of Pt(PPh<sub>3</sub>)<sub>4</sub> with different mole ratios are now successfully rationalized.

Although there is no direct evidence concerning the nature of the transition states involved in the oxidative addition of ICl to Pt(PPh<sub>3</sub>)<sub>4</sub> yielding trans-PtClI(PPh<sub>3</sub>)<sub>2</sub>, it would appear to be useful to speculate on the probable mechanism (Figure 20) involved in the reaction. In the solution, Pt(PPh<sub>3</sub>)<sub>3</sub> is assumed to be trigonal planar. Attack by ICl at the Pt atom is perpendicular to the trigonal plane. This is the preferred direction of attack which is the direction of the filled d<sub>z</sub><sup>2</sup> orbital of the Pt atom, such that a σ-bond can be formed between the metal atom and the incoming atom. At this time, electron transfer from the metal to ICl occurs with subsequent

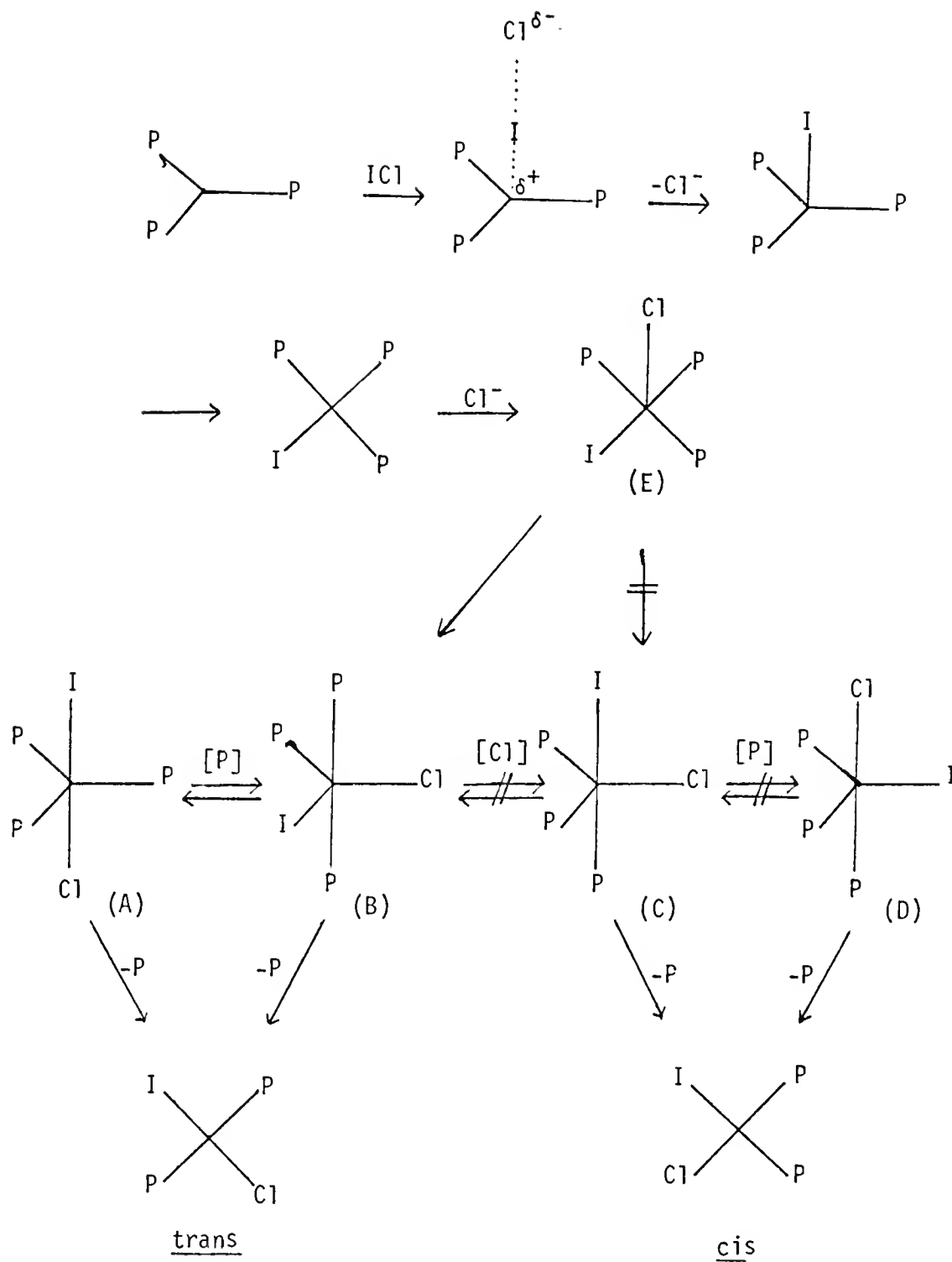
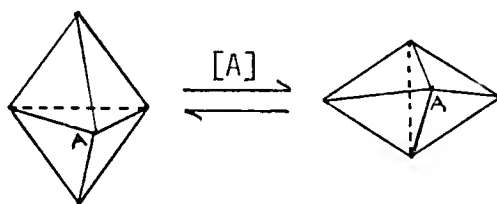


Figure 20. Proposed Mechanism for the Oxidative Addition to  $\text{ICl}$  to  $\text{Pt}(\text{PPh}_3)_3$  in the Absence of Free Phosphine

cleavage to form a distorted tetrahedron which collapses to a square planar configuration typical of Pt(II) complexes. A chloride ion then attacks the Pt atom along  $p_z$  perpendicular to the plane with subsequent formation of trigonal-bipyramidal species from which the product is obtained.

Pentacoordinated species have been detected spectrophotometrically in substitution reactions of  $\text{PtCl}_2(\text{NH}_3)_2$  by  $\text{NO}_2^-$ <sup>57</sup>, and are implicated in cis-trans isomerizations of Pt(II) complexes<sup>58,59</sup>. A characteristic property of trigonal-bipyramidal species is pseudorotation, which is defined as the intramolecular process whereby a trigonal-bipyramidal molecule is transformed by deforming bond angles in such a way that it appears to have been rotated by  $90^\circ$  about one of the trigonal-planar interatomic bonds. Thus, in the diagram below, the substituent A remains fixed while the apical substituents are pushed backward and the equatorial substituents pulled forward until the process leads to the second trigonal bipyramid, which appears to have been produced by rotating the first about the bond from the fixed substituent A (the "pivot") to the central atom. The symbol [A] is used to denote



pseudorotation with A as a pivot. By means of pseudorotation, substituents in apical positions are placed in equatorial positions and vice versa. From nmr studies on stabilities of possible positional isomers in a trigonal-bipyramidal structure containing different ligands, some empirical rules have been formulated with regards to the

preference of different ligands for either apical or equatorial sites<sup>60,61</sup>. Ligands which are strong  $\pi$ -acceptors ( $\text{CO}$ ,  $\text{SnCl}_3^-$ ) prefer equatorial sites, whereas, strong  $\sigma$ -donors ( $\text{H}^-$ ,  $\text{CH}_3^-$ ) and electronegative ligands favor apical positions. Those ligands which do not show a propensity to be a  $\pi$ -acceptor or a  $\sigma$ -donor ( $\text{PR}_3$ ) have no particular preference for either site. Moreover, the stability of positional isomers is dependent on steric interaction between ligands, more bulky groups favoring equatorial sites. On the bases of these rules, it can be seen in Figure 20 that, the square pyramidal structure (E) can only give rise to structure (B) which pseudorotates to (A) and from which the product trans- $\text{PtClI}(\text{PPh}_3)_2$  finally results. The product can also be obtained, though less likely, directly from (B). (C) and (D), which can give rise to cis- $\text{PtClI}(\text{PPh}_3)_2$ , are not formed from (E), (A) or (B) by fluxional changes because they are the higher energy forms of the possible position isomers on two counts: (1) Only one electronegative halide ligand is apical and (2) The three  $\text{PPh}_3$  ligands experience most steric repulsions with two of them in equatorial and the other at an apical position. Thus, on the basis of both electronegativity and steric effects, (C) and (D) are of higher energy than (A) and, probably, are also of higher energy than (B) on the basis of the overriding steric effect. Hence, no cis-isomers are formed.

When the  $\text{Pt}(0)$  species is  $\text{Pt}(\text{PPh}_3)_2$ , the mechanism is again the same if it is assumed that it is trigonal planar in solution as a consequence of solvation. It will be recalled that the rate of reaction of this species with  $\text{CH}_3\text{I}$  is several times faster than the rate of reaction of  $\text{Pt}(\text{PPh}_3)_3$  with the same halide. This can be accounted

for by the fact that  $\text{PPh}_3$  is a better  $\pi$ -acceptor than is the solvent molecule so that the greater electron density on the Pt atom in  $\text{Pt}(\text{PPh}_3)_2$  (solvent) makes it more nucleophilic and, hence, more reactive.

Alternatively if, in solution, the  $\text{Pt}(\text{PPh}_3)_2$  species is linear, the trans-product can be obtained if the  $\text{ICl}$  attacks and forms the trigonal planar  $\text{PtI}(\text{PPh}_3)_2^+$  with a subsequent attack of  $\text{Cl}^-$  from above the trigonal plane and finally, the collapse of the distorted tetrahedron into trans- $\text{PtClI}(\text{PPh}_3)_2$ .

The mechanism for the formation of trans- $\text{PtICH}_3(\text{PPh}_3)_2$  from  $\text{Pt}(\text{PPh}_3)_4$  and  $\text{CH}_3\text{I}$  can be postulated to follow a similar pathway.  $\text{CH}_3^-$  (a good  $\sigma$ -donor) and  $\text{I}^-$  (an electronegative ligand) both prefer apical positions and all the arguments advanced above obtain.

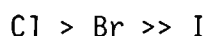
The reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{IBr}$  is analogous to that with  $\text{ICl}$ . Using a  $\text{Pt}(0)$  to  $\text{IBr}$  ratio of 1:1 and 1:6, cis- $\text{PtBrI}(\text{PPh}_3)_2$  and trans- $\text{PtBr}_2(\text{PPh}_3)_2$  (86%) are obtained, respectively. With the ratio of reactants intermediate between the above two mole ratios, e.g., 1:2, the product is an approximate mixture of cis- $\text{PtBrI}(\text{PPh}_3)_2$  and trans- $\text{PtI}_2(\text{PPh}_3)_2$ . Infrared spectroscopy of a reaction mixture containing an initial mole ratio of  $\text{Pt}(0)$  to  $\text{IBr}$  of 1:3 still indicates the presence of some cis-complex, cis- $\text{PtBrI}(\text{PPh}_3)_2$ . In terms of % yield and expediency, the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{ICl}$  in a 1:6 mole ratio, again provides a superior method of synthesis of trans- $\text{PtBr}_2(\text{PPh}_3)_2$  over any other published methods. The mechanism of the reaction is proposed to be similar to that of  $\text{Pt}(\text{PPh}_3)_3$  and  $\text{ICl}$  and will not be discussed further.

## Oxidative Addition of Halogens to Tetrakis(triphenylphosphine)platinum(0)

Customary reactions involving the oxidative addition of  $\text{Br}_2$  and  $\text{I}_2$  to  $\text{Pt}(\text{PPh}_3)_4$  have been reported either explicitly or implicitly to yield invariably cis- $\text{PtBr}_2(\text{PPh}_3)_2$  and  $\text{PtI}_2(\text{PPh}_3)_2$ , respectively.<sup>1,5,62,63</sup> Although no report of the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{Cl}_2$  has been reported, the general consensus among chemists in this research area is that cis- $\text{PtCl}_2(\text{PPh}_3)_2$  would result. This is evidenced by the fact that, hitherto, synthetic methods for the synthesis of trans- $\text{PtX}_2(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) involve either photochemical<sup>49</sup> or thermal isomerization<sup>36</sup> of the cis-isomers or from the reaction<sup>55</sup> of  $\text{PtHCl}(\text{PPh}_3)_2$  with  $\text{HgCl}_2$  (which gives a very low yield) instead of the obvious reaction of  $\text{Pt}(\text{PPh}_3)_4$  directly with the halogens. The first inkling that the addition of the halogens to  $\text{Pt}(\text{PPh}_3)_4$  might yield trans-dihalogenobis-(triphenylphosphine)platinum(II) came when the mechanism for the oxidative addition of  $\text{ICl}$  to  $\text{Pt}(\text{PPh}_3)_4$  (discussed earlier) was considered. It is recalled that the latter reaction yielded trans- $\text{PtClI}(\text{PPh}_3)_2$  as a consequence of the proposed energetically favored trigonal bipyramidal transition state,  $\text{PtClI}(\text{PPh}_3)_3$ , in which the electronegative halogen atoms occupy apical positions and the bulky triphenylphosphine ligands occupy equatorial positions. This more stable transition state can only yield trans- $\text{PtClI}(\text{PPh}_3)_2$  by elimination of  $\text{PPh}_3$  from an equatorial position. It became apparent that, if halogen is used instead of  $\text{ICl}$ , the most stable transition state in the oxidative addition to  $\text{Pt}(\text{PPh}_3)_4$  would also have to be one in which the electronegative halogens are apical and the three  $\text{PPh}_3$  ligands are at equatorial sites and that trans-isomers would result. The



fact that only cis-isomers have been reported must be because of isomerization, in the presence of triphenylphosphine, of the initially formed trans-isomer to the cis-isomer as in the case of trans-PtClI-(PPh<sub>3</sub>)<sub>2</sub>. This trans-cis isomerization has already been reported to occur rapidly for PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in chloroform<sup>55</sup>. This author has demonstrated that the rate of trans-cis isomerization in benzene for PtX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (X = Cl, Br or I) follows the order:



Thus, in order to demonstrate that the addition of halogens to Pt(PPh<sub>3</sub>)<sub>4</sub> is a trans-addition by isolating trans-isomers, the experimental conditions must be such that no free triphenylphosphine is present after the formation of trans-PtX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The phosphine-catalyzed trans-cis isomerization reaction can then be prevented.

One way to prevent isomerization of the trans-products is to "tie up" the free triphenylphosphine present in the reaction mixture by using more than the stoichiometric amount of halogen required for the oxidative-addition reaction. The excess halogen reacts with PPh<sub>3</sub> to form [PPh<sub>3</sub>X]X (and/or [PPh<sub>3</sub>X]X<sub>3</sub> depending on the amount of X<sub>2</sub> used). Previous investigators, who obtained cis-isomers, were reluctant to use an excess of the halogen, presumably for fear of further oxidation of the initially formed PtX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> to PtX<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>. However, it was found that the first oxidative addition of X<sub>2</sub> to Pt(PPh<sub>3</sub>)<sub>4</sub> proceeds faster than the second oxidative addition of X<sub>2</sub> to PtX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and by limiting the reaction time to 3 minutes or less, the formation of Pt(IV) complexes can be eliminated. For I<sub>2</sub> and Br<sub>2</sub>, the reaction with Pt(PPh<sub>3</sub>)<sub>4</sub> for 3 minutes using a 4:1 mole

ratio of halogen to Pt(0) complex was found to be sufficient to yield exclusively trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and trans-PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, respectively. The conditions were modified for the reaction of chlorine with Pt(PPh<sub>3</sub>)<sub>4</sub>. Since trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is more rapidly isomerized in the presence of PPh<sub>3</sub> than trans-PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, it was found necessary to add the Pt(PPh<sub>3</sub>)<sub>4</sub> solution in a fast dropwise fashion to an excess of a stirred benzene solution of Cl<sub>2</sub> so that at any given time during the addition, no free phosphine can be present in the solution. The reaction time was also limited to 1.0 minute to prevent oxidation to PtCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> since Cl<sub>2</sub> is more reactive with both Pt(PPh<sub>3</sub>)<sub>4</sub> and PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> than Br<sub>2</sub> or I<sub>2</sub> with the corresponding reactants. With all three halogens, no cis-isomers could be detected by ir spectroscopy in the products. Thus, the addition of the halogens to Pt(PPh<sub>3</sub>)<sub>4</sub> is demonstrated to be a trans-addition reaction. It is of interest to note that this demonstration also provides very convincing confirmation to the validity of the mechanism of the oxidative addition of ICl to Pt(PPh<sub>3</sub>)<sub>4</sub> proposed earlier.

The reaction of I<sub>2</sub> with Pt(PPh<sub>3</sub>)<sub>4</sub> was also repeated using the stoichiometric amount of reactants (1:1) for the formation of PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The reaction time was extended to 15 minutes. It was found that trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was formed in spite of the presence of free tri-phenylphosphine being present under these conditions. This demonstrates that trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> isomerizes rather slowly in the presence of PPh<sub>3</sub> and suggest strongly that earlier investigators had indeed obtained the trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> but thought that they had cis-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> instead. Their mistaken notion might have been the result of an analogy with

the result of  $\text{Cl}_2$  and  $\text{Br}_2$  with  $\text{Pt}(\text{PPh}_3)_4$  where cis-isomers are indeed formed under their conditions of a 1:1 mole ratio of the reactants.

With trans- $\text{PtI}_2(\text{PPh}_3)_2$  cis-trans isomerization appear to occur more readily instead of trans-cis isomerization. Mastin has reported<sup>36</sup> that the thermal isomerization of the cis-isomer occurs in a refluxing chloroform solution containing 2% ethanol. This author has found that the isomerization also proceeds in a refluxing solution of benzene and even in the solid state by heating at  $200^\circ$ . Thus, trans- $\text{PtI}_2(\text{PPh}_3)_2$  appears to be relatively more thermodynamically stable with respect to cis- $\text{PtI}_2(\text{PPh}_3)_2$  than trans- $\text{PtBr}_2(\text{PPh}_3)_2$  and trans- $\text{PtCl}_2(\text{PPh}_3)_2$  with respect to their respective isomers.

#### Substitution Reactions of Dihalogenobis(triphenylphosphine)platinum(II) Complexes

In previous discussion on the mechanism of the oxidative-addition reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{ICl}$  (1:6 mole ratio), it was proposed that initial oxidative addition produced trans- $\text{PtClI}(\text{PPh}_3)_2$  which then reacted with more  $\text{ICl}$  to form the final, isolated product trans- $\text{PtCl}_2(\text{PPh}_3)_2$ . It became necessary then, to perform the experiment involving the reaction of cis- $\text{PtClI}(\text{PPh}_3)_2$  with  $\text{ICl}$  in an attempt to demonstrate if indeed, this reaction would yield cis- $\text{PtCl}_2(\text{PPh}_3)_2$ . If this result obtains, then by analogy, the reaction of trans- $\text{PtClI}(\text{PPh}_3)_2$  with  $\text{ICl}$  would have to yield trans- $\text{PtCl}_2(\text{PPh}_3)_2$ . It is noted here that cis- $\text{PtClI}(\text{PPh}_3)_2$  was used out of necessity, because the trans-isomer was not isolated. Subsequent to this experiment, a number of reactions of cis- and trans- $\text{PtXY}(\text{PPh}_3)_2$  (X or Y = Cl, Br or I) with  $\text{ICl}$ ,  $\text{IBr}$  and  $\text{Br}_2$  were studied.

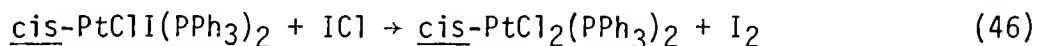
The complexes, cis-PtXY(PPh<sub>3</sub>)<sub>2</sub>, are only sparingly soluble in benzene and hence the reactions were carried out in either CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub> in which they are soluble. For the complexes, trans-PtX<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, benzene was used as the solvent. The general procedure which was followed involved the mixing of an ethereal solution of the interhalogen or halogen with a solution (C<sub>6</sub>H<sub>6</sub>, CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>, where appropriate) of PtXY(PPh<sub>3</sub>)<sub>2</sub> and stirring the mixture for 5-15 minutes. The reaction mixture was then concentrated to a small volume followed by addition of MeOH to effect more complete precipitation of the product. On subsequent recrystallization from benzene (for trans-products) or from chloroform-methanol (for cis-products), the pure products were obtained.

From the reactions of cis- and trans-PtXY(PPh<sub>3</sub>)<sub>2</sub> with interhalogens and halogens, the following observations are made: (1) The reactions are substitution reactions in which a less electronegative element is always replaced by a more electronegative one. For example, the reaction of cis-PtClI(PPh<sub>3</sub>)<sub>2</sub> and trans-PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with ICl yields cis- and trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, respectively. (2) The reactions are stereospecific, i.e., cis- and trans-reactants yield cis- and trans-products, respectively. This observed stereospecificity is in accord with all other substitution reactions of square-planar Pt(II) complexes. (3) Most of the reactions are completed in about 5 minutes at room temperature. The occurrence of such facile substitution reactions of Pt(II) complexes, which are well-known for their inertness, is surprising. (4) The yields are high (> 80%). (5) Under the reaction conditions which were employed, no oxidative addition of the interhalogen

or halogen to the Pt(II) forming Pt(IV) complexes is observed. This suggests that the substitution reactions occur faster than the oxidative-addition reactions.

Metathetical replacement of a halide ion by another in square-planar Pt(II) complexes have been reported.<sup>37</sup> However, the conditions for the displacement reactions involve heating and using a large excess of halides (up to 500-fold excess). Mastin has reported<sup>37</sup> the reaction of cis-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with KI and KBr yielding cis-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and cis-PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> respectively, by refluxing the mixture. The reactions of halogens with PtX<sub>2</sub>[P(n-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>2</sub> and PtX<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub> have also been reported but only to involve oxidative addition of the halogen to the Pt(II) complexes yielding PtX<sub>4</sub>[P(n-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>2</sub> and PtX<sub>4</sub>(AsPh<sub>3</sub>)<sub>2</sub>,<sup>65</sup> respectively. Thus, the facile substitution reactions between the Pt(II) complexes and the interhalogens or halogens are rather novel and surprising.

The driving force for the substitution reactions is most probably due to the formation of stronger Pt(II)-halogen bonds. Taking the reaction



as a case in point, the energetics involve the breaking of a Pt-I and an I-Cl bond and the formation of a Pt-Cl and an I-I bond. Since there is a net loss in energy with respect to the halogen-halogen bonds, [ $D(\text{I-Cl}) > D(\text{I-I})$ ], there must be a compensating gain in bond energy in the formation of the Pt-Cl bond. Indeed, the Pt(II)-X bond strengths have been demonstrated by mass spectral data to follow the order  $\text{M-I} < \text{M-Br} < \text{M-Cl}$ .<sup>37</sup> The same trend for other metals is indicated by vibrational<sup>66</sup> and thermodynamic<sup>67</sup> data.

The reaction of trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with ICl to yield trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> can be considered as resulting from a displacement by ICl on trans-PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> forming first trans-PtClI(PPh<sub>3</sub>)<sub>2</sub> followed by a second displacement by ICl on trans-PtClI(PPh<sub>3</sub>)<sub>2</sub> yielding finally trans-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

The alternative probability which can be considered and which can account for the products of the reactions of PtXY(PPh<sub>3</sub>)<sub>2</sub> with the interhalogen and halogen is via an oxidative addition-reductive elimination reaction. This alternative can be ruled out on the basis that under the mild reaction conditions used, a reductive elimination could not have occurred. This contention is supported by reports that analogous Pt(IV) complexes are stable under the reaction conditions. Trans-PtCl<sub>4</sub>(PPr<sup>n</sup>)<sub>3</sub>, for example, undergoes reductive elimination<sup>64</sup> at 195° and PtX<sub>4</sub>(AsPh<sub>3</sub>)<sub>2</sub> complexes melt without decomposition and can be boiled with alcohol or acetone without reduction taking place.<sup>65</sup>

Although the details of the mechanism cannot be established without more kinetic data, one can speculate on a reasonable mechanism for the reaction between cis-PtClI(PPh<sub>3</sub>)<sub>2</sub> and ICl as given in Figure 21. The reaction proceeds by electrophilic attack of the Pt(II) atom on the electronegative Cl end of the molecule, ICl. I<sup>+</sup> leaves and the ligand being displaced (I<sup>-</sup>) moves down below the original tetragonal plane to form the trigonal-bipyramidal transition state. Subsequent pseudorotation is a possibility but invoking pseudorotation would violate the rigid stereospecificity rule. Thus, it is assumed that as the leaving group (I<sup>-</sup>) must move further down below the original square plane until it is at the apex of the new square pyramid, followed by subsequent dissociation to yield the product, cis-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

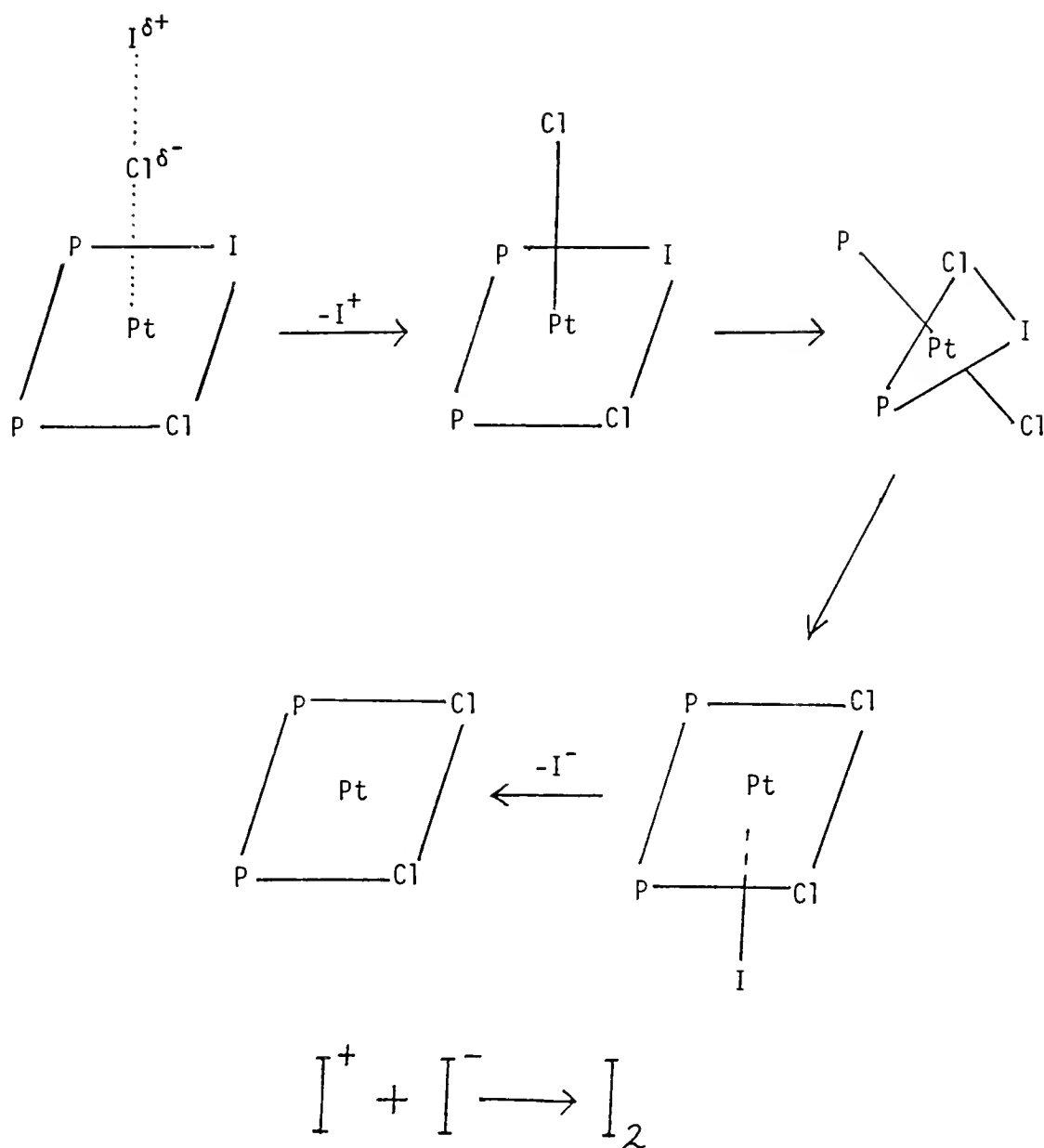


Figure 21. Proposed Mechanism for the Reaction of *cis*-PtClI(PPh<sub>3</sub>)<sub>2</sub> With ICl

The mechanisms of other displacement reactions can be similarly discussed. All the investigated reactions involving interhalogens and halogens are summarized in the scheme in Figure 22.



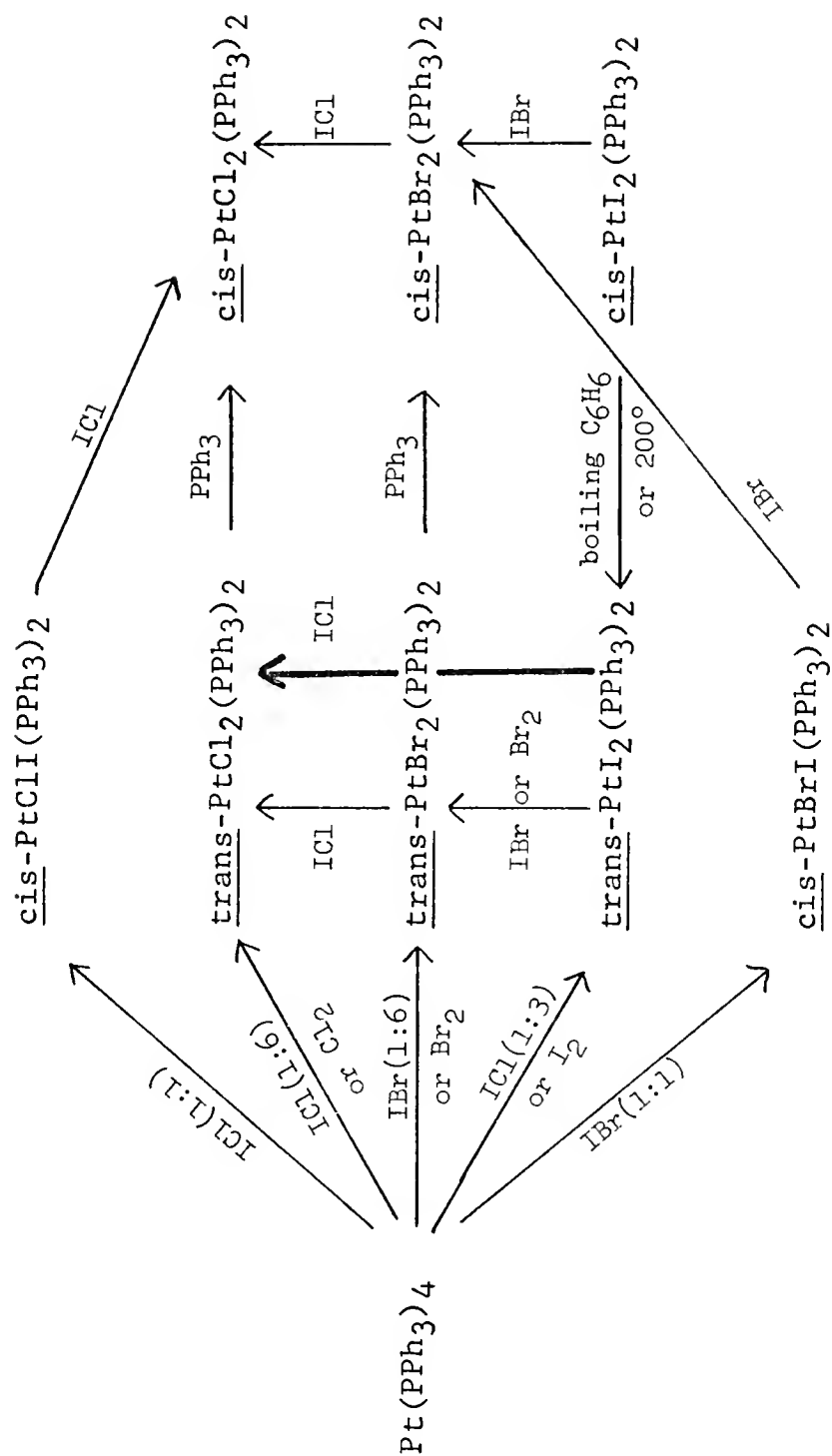


Figure 22. Scheme for the Reactions of Pt Complexes With Halogens and Interhalogens

## CONCLUSION

As mentioned earlier, the objectives of this work were: (1) the study and elucidation of the mechanism of the reactions between selected organic halides and  $\text{Pt}(\text{PPh}_3)_4$ , (2) the correlation of reactivity and mechanism with structural aspects of the addendum molecule, (3) the extension of analogous reactions to oxidative addition to  $d^8$  systems, and (4) the investigation of the possibility of generation of triarylmethyl radicals using  $\text{Pt}(\text{PPh}_3)_4$  instead of the classical method of Gomberg using "molecular" silver. From this study, the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with aromatic triarylmethyl halides,  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_2\text{CHBr}$ , has been established to proceed via a free-radical mechanism on the basis of activation parameter data and product studies. This free-radical mechanism is in contrast to the normal oxidative addition of  $\text{CH}_3\text{I}$  to  $\text{Pt}(\text{PPh}_3)_4$  yielding  $\text{PtICH}_3(\text{PPh}_3)_2$ . The reaction of these organic halides with a  $d^8$  complex,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , has also been found to react analogously via a free-radical pathway. On the question of dependence of reactivity and mechanism on structure, the conclusion is reached that only secondary and tertiary aromatic halides react via a free-radical pathway because of the relative stability of the radicals generated. For alkyl halides such as  $\text{CH}_3\text{I}$ , if a free-radical mechanism were operative, the generation of a relatively unstable radical,  $\text{CH}_3\cdot$ , would be energetically prohibitive. The rate of the investigated free-radical reactions appear to depend

directly on the C-halogen bond strength; the lower the bond strength, the faster the rate. The reaction of  $\text{Pt}(\text{PPh}_3)_4$  with triarylmethyl halides was also found to be a superior method than Gomberg's for the generation of triarylmethyl radicals. Thus, the objectives of this work seem to be completely fulfilled.

In the midst of the above studies, the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with interhalogens were investigated as a side-light to see how they would react in comparison to the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with the organic halides. This side-light subsequently developed beyond all expectations to contribute significantly to the overall quality and scope of this dissertation. The reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{ICl}$  was found to yield cis- $\text{PtClI}(\text{PPh}_3)_2$ , trans- $\text{PtI}_2(\text{PPh}_3)_2$  and trans- $\text{PtCl}_2(\text{PPh}_3)_2$ , respectively by merely varying the mole ratio of the reactants. The formation of such diverse products was successfully rationalized and a mechanism for the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{ICl}$  yielding trans- $\text{PtClI}(\text{PPh}_3)_2$  was proposed. This mechanism predicted that the oxidative addition of the halogens to  $\text{Pt}(\text{PPh}_3)_4$  should be a trans-addition despite numerous reports of the isolation of cis-products only. It was indeed satisfying and rewarding to verify this prediction under carefully-controlled conditions. A rapid and high-yield synthesis for trans- $\text{PtX}_2(\text{PPh}_3)_2$ , where  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ , was also developed from the reactions of  $\text{Pt}(\text{PPh}_3)_4$  with the interhalogens and halogens. Finally, the reactions of many supposedly inert dihalogenobis(triphenylphosphine)platinum(II) complexes with halogens and interhalogens were found to be facile substitution reactions which occur faster than the corresponding oxidative-addition reactions.

It can truly be asserted that much more than the initial objectives of this work have been accomplished. Although much has been done and many questions answered, the results of this work have opened up many research areas which merit investigation. For example, the kinetic studies on the reactions of  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$  and  $\text{RhX}(\text{CO})(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) with secondary and tertiary aromatic halides should provide details of the mechanism and information on effects of structure on the reactivity of the  $d^8$  complexes with the organic halides. Furthermore, the reactions of  $\text{Pt}(\text{PPh}_3)_4$  with halides which have been reported to yield cis-isomers should be reinvestigated to see if indeed the reactions are actually trans-additions forming trans-products which subsequently isomerized. The results of these and other investigations would surely further the understanding of oxidative-addition reactions.

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Tong Wai Lee was born on July 4, 1943, in Ipoh, Malaysia. He had his primary, secondary and tertiary education in Malaysian educational institutions graduating from the University of Malaya with a M.Sc. degree in June, 1970. In 1969, he was awarded a Fulbright-Hays Scholarship which enabled him to come to the United States where he began his studies towards a Ph.D. degree at the University of Florida. He has served as a teaching assistant and as an interim instructor in the Department of Chemistry and received the Duport Award for Excellence in Teaching for the year 1971-72.

Tong Wai Lee is married to the former Julie Tan and they have a child, Stanley.


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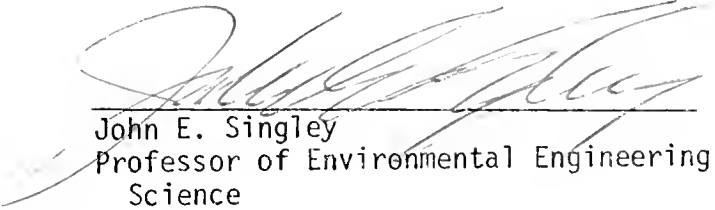
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